

Density Functional Analysis of the Spin Exchange Interactions in VOSb₂O₄

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The spin exchange parameters of VOSb₂O₄ were evaluated by performing energy-mapping analysis based on density functional calculations. The spin exchange interaction between the nearest-neighbor V⁴⁺ ions is strongly antiferromagnetic while other interactions are negligible. Thus, the magnetic structure of VOSb₂O₄ is best described by a spin-1/2 Heisenberg antiferromagnetic chain with no spin frustration.

Key Words : Spin exchange interactions, Mapping analysis, Density functional theory calculations, VOSb₂O₄

Introduction

The layered vanadium oxide VOSb₂O₄, synthesized by solid state reaction, crystallizes in the monoclinic space group C2/c with the unit cell dimensions $a = 18.03 \text{ \AA}$, $b = 4.800 \text{ \AA}$, $c = 5.497 \text{ \AA}$, and $\beta = 94.58^\circ$.¹ In VOSb₂O₄ the VO₅ square pyramids share their *trans* edges to form VO₃ ribbon chains running along the *c*-direction (Figure 1(a)). The basal O atoms of these ribbon chains are connected to Sb₂O₂ ribbon chains along the *a*-direction to form a layer of composition VOSb₂O₄, and such VOSb₂O₄ layers are stacked along the *b*-direction. Each V atom exists as a V⁴⁺ (d^1 , $S = 1/2$) ion with its magnetic orbital (*i.e.* the singly filled orbital) described by the *xy* orbital (Figure 1(b)). Thus, in describing the magnetic properties of VOSb₂O₄, it is natural to consider the nearest-neighbor intrachain exchange J_1 , the next-nearest neighbor intrachain exchange J_2 , and the interchain exchange J_3 depicted in Figure 1(a). Concerning the values of these parameters, there have been conflicting reports.^{2,3} The temperature-dependence of the magnetic susceptibility of VOSb₂O₄ shows a broad maximum at $T_{\text{max}} \approx 160 \text{ K}$, which is well reproduced by a spin-1/2 Heisenberg antiferromagnetic (AFM) chain with $J_1/k_B \approx 250 \text{ K}$.² (We use the convention that an AFM spin exchange is represented by a

positive number.) When two intrachain exchanges J_1 and J_2 are used, a poorer description of the observed magnetic susceptibility data results, so Pashchenko *et al.*² concluded that VOSb₂O₄ is a one-dimensional (1D) spin-1/2 Heisenberg AFM chain with no spin frustration. In their density functional analysis of the magnetic susceptibility of VOSb₂O₄, Chaplygin *et al.*³ carried out calculations for the non-magnetic (NM), ferromagnetic (FM) and AFM states of VOSb₂O₄ to find that the AFM state is lower in energy than the FM state by 14.2 meV per formula unit (FU). Thus, they obtained $J_1 = 330 \text{ K}$ by $\Delta E = E_F - E_{\text{AF}} = 2J_1$, and $J_1 = 238 \text{ K}$ by $\Delta E = J_1 \ln 2$ considering the quantum fluctuation in the AFM state. Since there is uncertainty as to how well density functional calculations include the effect of quantum fluctuations, Chaplygin *et al.* analyzed the electronic band structures of the NM and FM states in terms of tight-binding fits to deduce the hopping parameters t_i associated with the spin exchange paths J_i ($i = 1-3$). Using the empirical relationship $J_i = -4t_i^2/U$, they obtained $J_1 = 1786 \text{ K}$, $J_2 = 301 \text{ K}$, and $J_3 = 81 \text{ K}$. Although the relative values of these $J_1 - J_3$ appear to be reasonable, the J_1 value thus obtained is greater than the experimental estimate by a factor of ~ 7 . To date, all three exchange parameters $J_1 - J_3$ of VOSb₂O₄ have not been evaluated on the basis of density functional calculations. In the present work, we carry out energy-mapping analysis based on density functional theory (DFT) calculations to evaluate the spin exchange parameters $J_1 - J_3$ of VOSb₂O₄.

Computational Details

Our density functional calculations employed the projector augmented wave (PAW) method encoded in the Vienna ab initio simulation package (VASP),⁴⁻⁶ and the generalized-gradient approximation (GGA) of Perdew, Burke and Ernzenhof⁷ for the exchange-correlation functional with the plane-wave-cut-off energy of 450 eV and a set of $2 \times 6 \times 4$ k-points to cover the irreducible Brillouin zone. To examine the effect of electron correlation associated with the V 3d states, the DFT plus on-site repulsion method (DFT+U)⁸ was used with the effective U_{eff} values of 0-4 eV. To evaluate

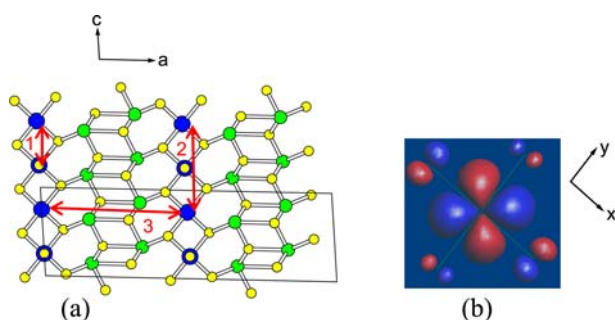


Figure 1. (a) Projection view of the crystal structure of VOSb₂O₄, where the blue, green and yellow circles represent V, Sb and O atoms, respectively. The numbers 1, 2 and 3 refer to the spin exchange paths J_1 , J_2 and J_3 , respectively. (b) Magnetic orbital *xy* of an isolated VO₅ square pyramid taken from VOSb₂O₄.

the spin exchange interactions of the next-nearest neighbor exchange J_2 , we used the (a, b, 2c) supercell for our calculations.

Mapping Analysis

The plots of the partial density of states (PDOS), calculated for the FM state of VOSb₂O₄, are presented in Figure 2, which shows that the up-spin xy states are the only V 3d states that are occupied. This is consistent with the electronic structure description that the V atoms exist in VOSb₂O₄ as V⁴⁺ (d¹) ions, and the magnetic orbital of V⁴⁺ (d¹) is the xy orbital.

The spin exchange interactions of a crystalline solid can be determined by energy-mapping analysis on the basis of first principles electronic density functional calculations for its ordered spin states.⁹⁻¹² Our approach is very different from that of Chaplygin *et al.*,³ although both rely on first principles DFT electronic structure calculations. In the tight-binding fitting analysis based on local spin-density approximation (LSDA) calculations,^{13,14} the electronic structure of a

magnetic insulator is described by the electronic energy band calculated for its normal metallic state, and the dispersion relations of the resulting partially filled bands are used to extract the hopping integrals needed for discussing the antiferromagnetic contribution J_{AF} to spin exchange interactions. Therefore, this approach leads to results quite similar to those of the spin dimer analysis based on extended Hückel tight binding (EHTB) calculations.⁹ Both approaches are limited in that the ferromagnetic contributions J_F to spin exchange interactions cannot be evaluated. In mapping analysis described below, we employ first principles DFT calculations to extract spin exchange parameters that contain both FM and AFM contributions. To evaluate three spin exchange parameters, $J_1 - J_3$ of VOSb₂O₄, we consider four ordered spin states, FM, AF1, AF2 and AF3, shown in Figure 3. The relative energies of these four states determined from our DFT+U calculations are summarized in Figure 3. The electronic structures of the FM, AF1, AF2 and AF3 states show an energy gap for all U ($= 0-4$ eV) values employed. The energies of these states can also be described in terms of the spin Hamiltonian,

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

where $J_{ij} = J_1 - J_3$. By applying the energy expressions obtained for spin dimers with N unpaired spin per spin site ($N = 1$ for VOSb₂O₄), the total spin exchange energies, per eight formula units (FUs), of the four ordered spin states are written as,^{9,15,16}

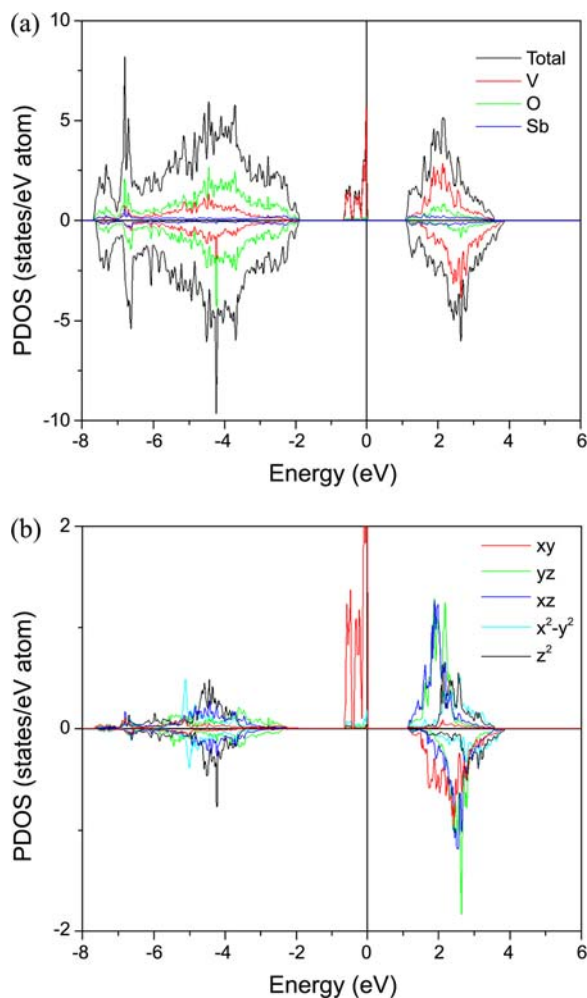


Figure 2. PDOS plots calculated for (a) the V, O and Sb atoms and for (b) the V 3d states of VOSb₂O₄, which are obtained from the DFT+U (with $U = 1$ eV) calculations for the FM state.

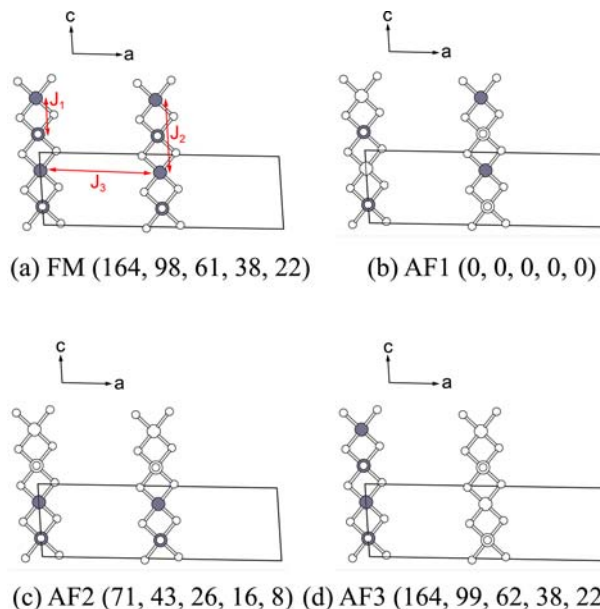


Figure 3. Ordered spin arrangements of VOSb₂O₄, where the large gray and white circles represent the up-spin and down-spin V⁴⁺ ion sites, respectively. The small white circles indicate O atoms. The red arrows represent the spin exchange paths $J_1 - J_3$. In each state, the numbers in parenthesis, from the left to right, are the relative energies (in meV per eight FUs) with respect to the AF1 state obtained from the DFT+U calculations with $U = 0, 1, 2, 3$, and 4 eV, respectively.

Table 1. Spin exchange parameters (in K) and Curie-Weiss temperature (in K) of VOSb₂O₄ obtained from DFT+U calculations

U	0 eV	1 eV	2 eV	3 eV	4 eV
J ₁ /k _B	476	286	179	111	64
J ₂ /k _B	32	18	12	9	7
J ₃ /k _B	0	1	1	1	0
J ₂ /J ₁	0.07	0.06	0.07	0.08	0.11
θ	-254	-152	-96	-60	-36

$$\begin{aligned}
 E_{\text{FM}} &= (8J_1 + 8J_2 + 16J_3) \left(\frac{N^2}{4} \right) \\
 E_{\text{AF1}} &= (-8J_1 + 8J_2 - 16J_3) \left(\frac{N^2}{4} \right) \\
 E_{\text{AF2}} &= (-8J_2 + 16J_3) \left(\frac{N^2}{4} \right) \\
 E_{\text{AF3}} &= (+8J_1 + 8J_2 - 16J_3) \left(\frac{N^2}{4} \right). \quad (2)
 \end{aligned}$$

By mapping the relative energies of the four ordered spin states determined by the DFT+U calculations onto the corresponding relative energies determined from the above spin exchange energies, we obtained the values of J₁ – J₃ summarized in Table 1, which shows that J₁ is AFM and is dominant for all cases of DFT+U calculations, J₂ is AFM and is substantially weaker than J₁, and J₃ is negligible. The ratio J₂/J₁, which is a measure for the intrachain spin frustration, is negligibly small. For example, J₂/J₁ ≈ 0.06 in the DFT+U calculations with U = 1 eV, which is considerably smaller than 0.17 estimated by Chaplygin *et al.* from their tight-binding analysis.³ Therefore, VOSb₂O₄ is best described by a spin-1/2 Heisenberg AFM 1D chain without frustration, as suggested by Pashchenko *et al.*²

To know how reasonable the calculated J₁ – J₃ values are, we calculate the Curie-Weiss temperature θ of VOSb₂O₄ using them. Within the mean-field theory,¹⁷ θ is related to the spin exchange parameters J₁ – J₃ as follows:

$$\theta = \frac{S(S+1)}{3k_B} \sum_i z_i J_i \approx \frac{(J_1 + J_2)}{2k_B}$$

The evaluated θ is summarized in Table 1. The experimental value θ = -188 K¹ is well reproduced by using the spin exchange parameters obtained from our DFT+U calculations with U = 1 eV.

Conclusions

Our calculations for VOSb₂O₄ show that J₁ is strongly AFM and dominant, J₂ is AFM but substantially weaker than the J₁, and the interchain spin exchange J₃ is negligible. The experimental Curie-Weiss temperature of VOSb₂O₄ (*i.e.*, -188 K) is best reproduced by using the set of J₁ – J₃ values obtained from the DFT+U calculations with U = 1 eV. Thus, the magnetic properties of VOSb₂O₄ are best described by a spin-1/2 AFM 1D chain with no spin frustration.

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