Density Functional Analysis of the Spin Exchange Interactions in VOSb$_2$O$_4$

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The spin exchange parameters of VOSb$_2$O$_4$ were evaluated by performing energy-mapping analysis based on density functional calculations. The spin exchange interaction between the nearest-neighbor V$^{4+}$ ions is strongly antiferromagnetic while other interactions are negligible. Thus, the magnetic structure of VOSb$_2$O$_4$ 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, VOSb$_2$O$_4$

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**Introduction**

The layered vanadium oxide VOSb$_2$O$_4$, synthesized by solid state reaction, crystallizes in the monoclinic space group C2/c with the unit cell dimensions $a = 18.03$ Å, $b = 4.800$ Å, $c = 5.497$ Å, and $\beta = 94.58^\circ$. In VOSb$_2$O$_4$ the VO$_4$ square pyramids share their trans edges to form VO$_3$ ribbon chains running along the c-direction (Figure 1(a)). The basal O atoms of these ribbon chains are connected to Sb$_2$O$_3$ ribbon chains along the a-direction to form a layer of composition VOSb$_2$O$_4$, and such VOSb$_2$O$_4$ layers are stacked along the b-direction. Each V atom exists as a V$^{4+}$ (i.e. the singly filled orbital) described by the xy orbital (Figure 1(b)). Thus, in describing the magnetic properties of VOSb$_2$O$_4$ 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.\(^5\)\(^6\) The temperature-dependence of the magnetic susceptibility of VOSb$_2$O$_4$ shows a broad maximum at $T_{\text{max}} = 160$ K, which is well reproduced by a spin-1/2 Heisenberg antiferromagnetic (AFM) chain with $J_1/k_B \approx 250$ 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.\(^7\) concluded that VOSb$_2$O$_4$ 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 VOSb$_2$O$_4$, Chaplygin et al.\(^3\) carried out calculations for the non-magnetic (NM), ferromagnetic (FM) and AFM states of VOSb$_2$O$_4$ 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 $J_1 = 330$ K by $\Delta E = E_F - E_{AF} = 2J_1$, and $J_1 = 238$ K by $\Delta E = J_1\ln2$ 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 $J_1 = 1786$ K, $J_2 = 301$ K, and $J_3 = 81$ K. Although the relative values of these $J_1$ and $J_3$ 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 VOSb$_2$O$_4$ 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 VOSb$_2$O$_4$.

**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 Ernzerhof\(^5\) 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
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 VOSb$_2$O$_4$, 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 VOSb$_2$O$_4$ as V$^{4+}$ (d$^1$) ions, and the magnetic orbital of V$^{4+}$ (d$^1$) 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. Our approach is very different from that of Chaplygin et al., although both rely on first principles DFT electronic structure calculations. In the tight-binding fitting analysis based on local spin-density approximation (LSDA) calculations, 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. 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 VOSb$_2$O$_4$, 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,

$$\hat{H} = \sum_{i<j} J_{ij} \hat{S}_i \cdot \hat{S}_j$$

(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 VOSb$_2$O$_4$), the total spin exchange energies, per eight formula units (FUs), of the four ordered spin states are written as.

**Figure 2.** PDOS plots calculated for (a) the V, O and Sb atoms and for (b) the V 3d states of VOSb$_2$O$_4$, which are obtained from the DFT+U (with U = 1 eV) calculations for the FM state.

**Figure 3.** Ordered spin arrangements of VOSb$_2$O$_4$, where the large gray and white circles represent the up-spin and down-spin V$^{4+}$ 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 VOSbO₄ obtained from DFT+U calculations

<table>
<thead>
<tr>
<th>U</th>
<th>0 eV</th>
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<th>2 eV</th>
<th>3 eV</th>
<th>4 eV</th>
</tr>
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<tbody>
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<td>J₁/kB</td>
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<td>286</td>
<td>179</td>
<td>111</td>
<td>64</td>
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<td>J₂/kB</td>
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<td>18</td>
<td>12</td>
<td>9</td>
<td>7</td>
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<td>1</td>
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<td>0</td>
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<tr>
<td>J₃/J₁</td>
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<td>0.06</td>
<td>0.07</td>
<td>0.08</td>
<td>0.11</td>
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<td>θ</td>
<td>−254</td>
<td>−152</td>
<td>−96</td>
<td>−60</td>
<td>−36</td>
</tr>
</tbody>
</table>

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. Therefore, VOSbO₄ 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 VOSbO₄ using them. Within the mean-field theory, θ is related to the spin exchange parameters J₁ − J₃ as follows:

\[
θ = \frac{S(S+1)}{3k_B} \sum_i z_i J_i = \frac{(J_1 + J_3)}{2k_B}
\]

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 VOSbO₄ 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 VOSbO₄ (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 VOSbO₄ are best described by a spin-1/2 AFM 1D chain with no spin frustration.

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References