Dzyaloshinskii-Moriya interaction in NaV₂O₅: a microscopic study.

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We present a unified account of magnetic exchange and Raman scattering in the quasi-one-dimensional transition-metal oxide NaV₂O₅. Based on a cluster-model approach explicit expressions for the exchange integral and the Raman-operator are given. It is demonstrated that a combination of the electronic-structure and the Dzyaloshinskii-Moriya interaction, allowed by symmetry in this material, are responsible for the finite Raman cross-section giving rise to both, one- and two-magnon scattering amplitudes.

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I. INTRODUCTION

More than four decades ago, Dzyaloshinskii and Moriya showed that the inclusion of spin-orbit coupling into the description of low-symmetry magnetic systems generates an anisotropic exchange interaction, the so-called Dzyaloshinskii-Moriya (DM) interaction.

In the early nineties, this interaction was discussed intensively in connection with the copper-oxide compounds. In particular, La₂CuO₄ exhibits a small gap in the spin-wave spectrum and a finite net ferromagnetic moment in each plane due to an out-of-plane canting of the spins. These features were attributed to DM interactions. Yildirim et al. did a careful microscopic study of this mechanism for tetragonal copper-oxide systems. In particular, their analysis proved that the orthorhombic distortion present in these materials is irrelevant to the out-of-plane magnetic anisotropy. Moreover, they showed that not only the antisymmetric anisotropic superexchange between two neighboring spins is important but the symmetric one as well.

The DM interaction has gained renewed interest in the context of the novel transition-metal oxide NaV₂O₅, which is believed to be a quarter-filled ladder compound in its high-temperature phase. At $T_C = 34$ K a phase transition, the interpretation of which is still controversial, takes place in this material where charge ordering ($2V^{+4.5} \rightarrow V^{+4} + V^{+5}$) occurs simultaneously with the opening of a spin-gap of approximately 10 meV. A series of recent studies has addressed the nature of the low-temperature state.

In this context it is of interest that very recent Electron Spin Resonance (ESR) experiments have detected a considerable anisotropy of the absorption intensity with respect to the magnetic field orientation, which has been attributed to the DM interaction. Apart from ESR, Raman scattering in the presence of a magnetic field is an alternative experiment for the observation of possible effects due to DM interactions. Unfortunately however, at present, the various experimental settings in search for such effects in Raman scattering have been unsuccessful for NaV₂O₅. This may not be conclusive yet, since the Raman cross section of the relevant scattering process could be too small to be observable.

In order to shed some light onto this scene, a microscopic analysis of the magnetic exchange and Raman scattering-operator seems highly desirable. However, apart from early work specific to the copper-oxides superconductors, such analysis is lacking. Therefore, it is the purpose of this paper to present a detailed description of the Raman operator for NaV₂O₅. In this context particular emphasis will be given to the role of the DM interaction which by symmetry is allowed in this material.

![Crystal structure of NaV₂O₅](image)

FIG. 1. Crystal structure of NaV₂O₅ in the high-temperature phase. The star denotes the location of the center of inversion, the dashed lines the constituting V-O-V ladders.
II. HAMILTONIAN

Above the spin-charge transition temperature $T_C$ NaV$_2$O$_5$ crystallizes in the centrosymmetric Pnmm space group.\footnote{The compound consists of VO$_5$ square pyramids sharing edges in the $ab$ layer and chains of Na located between the $ab$ layers. The superexchange interaction between vanadium sites is mediated through the pyramid’s base oxygens and the relevant structural element of NaV$_2$O$_5$ can be thought of consisting of ladders of V-O-V rungs along $b$ which are weakly coupled along $a$ (see Fig. 3).}

Discarding single-ion anisotropy, a general form of any scalar two-spin interaction between consecutive rungs along the $b$-direction of the ladder in NaV$_2$O$_5$ consists of two contributions

$$H^{(S)} = J H^{(Heis)} + D H^{(DM)}$$

i.e. the isotropic Heisenberg exchange $H^{(Heis)}$ and the Dzyaloshinskii-Moriya interaction $H^{(DM)}$:

$$H^{(Heis)} = \sum_l S_l \cdot S_{l+1},$$

$$H^{(DM)} = \sum_l \mathbf{e} \cdot (S_l \times S_{l+1})$$

where $S_l$ denotes the total spin on rung $l$. The form of the Dzyaloshinskii-Moriya (DM) vector $\mathbf{e}$ is determined by requiring that the energy of any configuration of spins has to be invariant under the symmetry transformations of the crystal structure. In our case, crystallography allows for a DM vector along $c$, i.e. $\mathbf{e} = (0,0,1)$. Note that this vector is defined locally in each unit cell and is not forbidden by the inversion center of the crystal structure, which lies in between two V-O-V ladders (see Fig. 4).

The standard derivation of (3) for the case of magnetic moments localized at single ionic sites can be found in the literature.\footnote{The hybridization matrix elements in Eq. (3) are: (i) $t_{\downarrow \perp}$ which denotes the direct hopping of electrons between the V-$d_{x^2-y^2}$ orbitals on sites 1 and 2 on a rung, (ii) $t_{dp}$ which denotes the charge transfer integral between the V-$d_{x^2-y^2}$ and O(1)-$p_y$ orbitals on a rung, (iii) $t_{\sigma} = -t_{||} + i \sigma \lambda$ is the hopping of electrons with spin $\sigma = \pm 1$ between the V-$d_{x^2-y^2}$ orbitals on two consecutive rungs along the ladder direction $b$. The spin-dependence of this hopping-integral is allowed due to the lack of a center of inversion in-between two rungs and arises from the spin-orbit coupling of strength $\lambda$, where $\lambda \sim \lambda$. The transfer matrix-elements $t_{\sigma}$ are diagonal in the spin quantum numbers because we have chosen the quantization axis for the spin to be along $c$, i.e. the main crystallographic axis, and finally (iv) $t_{pp}$ denotes the hopping of electrons between O(1)-$p_y$ orbitals on two consecutive rungs along $b$. The spin-dependence of $t_{pp}$ is small and will be discarded in the remainder of this paper.}

The parameters involved in (3) have been estimated\footnote{Substituting the electronic model-parameters cited in the previous section into Eqs. (A13) and (A15) we obtain $J \approx 0.049 eV \approx 560 K$ which agrees very well with the experimental value\footnote{The Coulomb repulsion $U$ leads to the formation of local moments on the rungs and in the following we will study the interaction between these local moments. For simplicity we consider the case $U \to \infty$, since we expect that any finite $U$ will lead to qualitatively similar results while increasing the complexity of the calculation needlessly.}} to be $\epsilon_p \approx -3 eV$, $t_{\perp \perp} \approx 0.25 eV$, $t_{dp} \approx -1 eV$, $t_{||} \approx -0.175 eV$, $t_{pp} \approx 0.5 eV$ and $U \approx 2.8 eV$. The Coulomb repulsion $U$ leads to the formation of local moments on the rungs and in the following we will study the interaction between these local moments. For simplicity we consider the case $U \to \infty$, since we expect that any finite $U$ will lead to qualitatively similar results while increasing the complexity of the calculation needlessly.

III. EXCHANGE COUPLINGS

As a first step towards the evaluation of the exchange couplings $J$ and $D$, we diagonalize the hamiltonian $H_0$ for an isolated rung. The ground state belongs to the 3-particle subspace. In addition, for the calculation of the exchange matrix elements, intermediate states in the 2- and 4-particle sector on a rung are required. Details of the derivation of the relevant eigenstates and eigenvalues of this cluster problem are stated explicitly in Appendix A. The exchange matrix elements are obtained by considering the process which describes a spin-flip between two consecutive rungs up to second order perturbation theory in $H_1$, as defined by $J^+$ and $J^-$ in Eq. (3). In particular,

$$J = \frac{1}{2}(J^+ + J^-) = Re(J^+)$$

Substituting the electronic model-parameters cited in the previous section into Eqs. (A13) and (A15) we obtain $J \approx 0.049 eV \approx 560 K$ which agrees very well with the experimental value$^{23}$ of $J_0 \approx 560K$. 

\[H_0 = \sum_{l,\sigma} \left( t_{\downarrow \downarrow} d^\dagger_{l+1,\sigma} d_{l,\sigma} + t_{dp}(d^\dagger_{l,\sigma} + d^\dagger_{l+1,\sigma})p_{l,\sigma} + c.c. \right)\]

\[+ \epsilon_p \sum_{l,\sigma} p^\dagger_{l,\sigma} p_{l,\sigma} + U \sum_{l,\sigma} d^\dagger_{l,\sigma} d_{l,\sigma} c.c. \]
Noting that \( t_4 = t_4^* \) and that \( \mathbf{D} \cdot (\mathbf{S}_j \times \mathbf{S}_{j+1}) = (D/2i) (S_j^- S_{j+1}^+ - S_{j+1}^- S_j^+) \), we have

\[
D = \frac{1}{2i} (J^+ - J^-) = Im(J^+)
\]

for the DM-coupling. Moriya has estimated that the order of magnitude of \( g \) where \( \omega \) is the deviation from the free-electron value. By considering \( \omega \) we evaluate \( D \) as a function of \( \lambda \), i.e. \( \lambda \approx 1meV \).

\[ \text{IV. RAMAN SCATTERING} \]

Fleury and Loudon have shown that light scattering from a spin system, depending on the polarization geometry of the incoming and outgoing electric fields, can lead to inelastic photon-induced superexchange. This has established Raman scattering as an important probe to obtain information on the local exchange dynamics in magnetic systems complementary to inelastic neutron scattering (INS). In the following we will generalize the early ideas of Fleury and Loudon to the case of NaV\(_2\)O\(_5\) clarifying the role of the DM interaction. In particular we find that in the case of a polarization of both, the incoming and outgoing photon fields parallel to \( b \), i.e. along the legs of the ladder, the Raman scattering operator \( H^{(R)} \) can be expressed as

\[
H^{(R)}(\omega_{in,out}) = J_R(\omega_{in,out}) H^{(Heis)} + D_R(\omega_{in,out}) H^{(DM)}
\]

where the \( \omega_{in} \) and \( \omega_{out} \) are the frequencies of the incoming or outgoing photons. The microscopic derivation \( H^{(R)}(\omega_{in,out}) \) is placed into the appendix. It is identical to that of the magnetic exchange integral with however the virtual hopping into the intermediate state of the exchange process driven by the coupling of the vector potential \( \mathbf{A} = (0, A_0, 0) \) to the current operator \( \mathbf{j} \cdot \mathbf{A} \) i.e. \( \mathbf{H}_1 \) of (3) has to be replaced by \( \mathbf{j} \cdot \mathbf{A} \) with the current operator \( \mathbf{j} = (j_a, j_b, j_c) \),

\[
j_b = i e \sum_{l,\sigma} \left( t_{pp} [p_l^\dagger p_{l+1}\sigma - p_{l+1}\sigma p_l^\dagger] + \sum_{\alpha} \left[ t_{l\alpha} d_{l\alpha,\sigma}^d d_{l+1\alpha,\sigma} - t_{l\alpha}^* d_{l+1\alpha,\sigma}^d d_{l\alpha,\sigma}^\dagger \right] \right).
\]

The total magnetic Raman scattering amplitude is then given up to second order in \( j_b/e \) by Eq. (A10) of Appendix A. From this, the definition of \( J_R(\omega_{in,out}) \) and \( D_R(\omega_{in,out}) \) is analogous to (3) and (4).

\[
J_R(\omega_{in,out}) = Re(R^- + (\omega_{in,out}))
\]

\[
D_R(\omega_{in,out}) = Im(R^- + (\omega_{in,out}))
\]

Note that a magnetic Raman process is possible only if \( H^{(R)}(\omega_{in,out}) \) induces transitions between different eigenstates of \( H^{(S)} \) i.e. if

\[
[H^{(R)}(\omega_{in,out}), H^{(S)}] = (J_R(\omega_{in,out}) D - D_R(\omega_{in,out})) J [H^{(Heis)}, H^{(DM)}] \neq 0
\]

\( \text{From (3) we conclude that magnetic Raman scattering from NaV}_2\text{O}_5 \) if modeled by (3) arises because two conditions are simultaneously satisfied. First, the existence of a spin-orbit coupling leads to a non-vanishing commutator in (3). Second, because the number of available paths for the magnetic and the photon induced exchange is larger than one and because \( \omega_{in/out} \neq 0 \) the factor of \( J_R(\omega_{in,out}) D - D_R(\omega_{in,out}) J \) is nonzero. The latter is true despite the formal similarity between the Raman scattering amplitude and the magnetic exchange integral, because \( H^{(R)}(\omega_{in,out}) \) displays an additional dependence on the photon energies. More specifically, for a single exchange path \( J_R(\omega_{in/out}) D - D_R(\omega_{in,out}) J = 0 \) for any value of \( \omega_{in/out} \) while for more than one exchange path \( J_R(\omega_{in/out}) D - D_R(\omega_{in,out}) J \) vanishes only at \( \omega_{in/out} = 0 \).

Next, we would like to point out that from the two terms, \( H^{(Heis)} \) and \( H^{(DM)} \) which make up \( H^{(R)}(\omega_{in,out}) \) it is actually \( H^{(DM)} \) which drives the magnetic Raman process. Up to now we have only considered anisotropic contributions to \( H^{(S)} \) to leading order in \( \lambda \). Kaplan and Shekhtman et al. have shown that, in general, the next-order term \( H^{(KSAE)} \sim \sum_l (e \cdot \mathbf{S}_l)(e \cdot \mathbf{S}_{l+1}) \) contributes to the spin Hamiltonian with a very specific prefactor:

\[
H^{(S)} = J H^{(Heis)} + D H^{(DM)} + (\sqrt{J^2 - D^2} - J) H^{(KSAE)}.
\]

Using this it is possible to transform \( H^{(S)} \) into an equivalent Hamiltonian of the plain Heisenberg form using the unitary mapping

\[
\tilde{S}_i^x = \cos \varphi_i S_i^x - \sin \varphi_i S_i^y \]

\[
\tilde{S}_i^y = -\sin \varphi_i S_i^x + \cos \varphi_i S_i^y
\]

with \( \tilde{S}_i^z = S_i^z \), \( \varphi_i = 2\varphi_0 \), and \( \tan(2\varphi_0) = D/J \). Expressed in terms of \( \tilde{S}_i \) the Hamiltonian reads \( \tilde{H}^{(S)} = \sqrt{J^2 - D^2} \sum_l \tilde{S}_l \cdot \tilde{S}_{l+1} \). Now, we note that higher order terms in \( \lambda \) will also contribute to the Raman operator. However, following the discussion after (3) it is obvious that (11) will not simultaneously reduce \( H^{(S)} \) and \( H^{(R)}(\omega_{in,out}) \) to a canonical Heisenberg form. Therefore, in the new basis, the Raman operator takes on the form \( \tilde{H}^{(R)}(\omega_{in,out}) = \tilde{J}_R(\omega_{in,out}) \tilde{H}^{(Heis)} + \tilde{D}_R(\omega_{in,out}) \tilde{H}^{(DM)} + O(\lambda^2) \). The only part of \( H^{(R)}(\omega_{in,out}) \) which does not commute with \( H^{(S)} \) to lowest order in \( \lambda \) is the DM-interaction, i.e. \( H^{(R)}(\omega_{in,out}) \equiv \tilde{D}_R(\omega_{in,out}) \tilde{H}^{(DM)}. \)
This completes our derivation of the Raman operator for the homogeneous phase of NaV$_2$O$_5$ as realized for $T > T_C$. Quite generally the preceding demonstrates that a DM-contribution to the Raman operator $H^{(R)}(\omega_{in,out})$ will occur in multiband systems whenever a DM exchange-interaction is allowed locally. Obviously it is tempting to analyse the effects of this form of $H^{(R)}(\omega_{in,out})$ also on a dimerized spin-liquid state, as present in NaV$_2$O$_5$ for $T < T_C$ and similarly in CuGeO$_3$ for $T < T_{SI}$. To this end let $H^{(R)}(\omega_{in,out})$ act on a pure dimer state $|\Phi_0\rangle = |s_1...s_\mu...\rangle$, where $\mu$ labels nearest-neighbor pairs of spins which are in a relative singlet state $|s_\mu\rangle$ - for the case of NaV$_2$O$_5$ these pairs of spins correspond to pairs of rungs $(2l, 2l + 1)$. One obtains

$$H^{(DM)}|\Phi_0\rangle = \sum \mu \left( -|2\mu|...t^{\mu}_p... - |...t^{\mu}_p|_{\mu+1}... \right) + |...t^{\mu}_p|_{\mu+1}... ) \right). \quad (12)$$

Here $|t^{\mu}_p\rangle (\alpha = x, y, z)$ refers to triplet states on the dimer-bonds. While the 2nd and 3rd term on the rhs. of (12) comprise of the usual total-spin zero, two-magnon excitation, the first term refers to a single-triplet state of only $z$-direction. This shows that single-magnon Raman-excitations are allowed in the presence of the DM-interaction. A single-magnon Raman line of this type has a clear experimental signature: it should show no splitting in an external magnetic field parallel to e (here along $z$) and it should split into two branches for a field perpendicular to the DM-vector. To our knowledge this signature has not yet been observed in experiment.

V. CONCLUSIONS

Motivated by recent ESR experiments[34] which probe the existence of a DM interaction in NaV$_2$O$_5$, we have presented a microscopic study of the possible impact of this interaction on the Raman process. We have derived the Raman operator in the homogeneous state of NaV$_2$O$_5$ and, additionally, have discussed its effect in the dimerized state.

In the dimerized state two Raman-modes have been observed in NaV$_2$O$_5$ in bb-polarization at 66cm$^{-1}$ and 104cm$^{-1}$. Tentatively these modes have been ascribed to magnetic bound states of total-spin zero [32]. On the other hand, for $T < T_C$, INS displays two well defined magnon-excitations, the energies of which, if properly zone-folded to zero momentum, coincide with the aforementioned two Raman modes [32]. Yet, Raman experiments show no indication of a splitting of these modes in an external magnetic field. We therefore conclude that the Raman modes should result from a two-magnon process (see [3]).

Clear evidence for a DM-vector in NaV$_2$O$_5$ along the $z$-direction has been provided by ESR experiments[32]. While these authors have interpreted these findings in terms of quasi-static charge-fluctuations above $T_C$, we believe, in view of the results presented here, that such an interpretation of the ESR-data is not necessary. In fact, the ESR-experiments can be understood in terms of the local DM-vector present also in the high-temperature phase.

In conclusion we have pointed out, that a local DM-vector gives rise to a non-trivial DM-contribution to the magnetic Raman-process whenever at least two non-equivalent exchange paths exist between the two magnetic moments considered. We have presented an explicit evaluation of this DM-contribution to the Raman operator for the case of the quarter-filled ladder compound NaV$_2$O$_5$ and we have shown, that one- and two-magnon processes arise naturally within this scenario. We have obtained estimates for the exchange-coupling constant along the b-direction in good agreement with experiment. Moreover we have evaluated the spin-orbit coupling constant within our cluster-approach. Finally, we note that evidence for DM-interactions in the two-dimensional dimer-compound SrCu$_2$(BO$_3$)$_2$[32] have been found by ESR[32] and far-infrared spectroscopy[34]. Therefore one might speculate if one-magnon Raman modes with the special signature described in the previous section could be observable in SrCu$_2$(BO$_3$)$_2$.

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APPENDIX A: EXCHANGE INTEGRAL AND RAMAN AMPLITUDE

In this appendix we present details of the evaluation of the 2, 3, and 4-particle eigenstates on a rung as well as the matrix elements relevant to the exchange integral and the Raman operator. We begin with the 3-particle space on rung $l$, which, in the subspace of no double-occupancy of the $d$-levels and total-spin $z$-component $S_z = \uparrow$ can be created by

$$3_1^{\uparrow\uparrow} = d^1_{\uparrow\uparrow}d^1_{\uparrow\uparrow\uparrow}p^1_{\uparrow\uparrow} \quad 3_2^{\uparrow\downarrow} = d^1_{\uparrow\downarrow}d^1_{\uparrow\uparrow\uparrow}p^1_{\uparrow\uparrow}$$
$$3_3^{\uparrow\downarrow} = d^1_{\uparrow\downarrow}d^1_{\uparrow\downarrow\uparrow}p^1_{\uparrow\downarrow} \quad 3_4^{\uparrow\downarrow} = d^1_{\uparrow\downarrow}d^1_{\uparrow\downarrow\uparrow}p^1_{\uparrow\downarrow} \quad (A1)$$

The set of corresponding states with $S_z = \downarrow$, is obtained by reversing $\uparrow$ to $\downarrow$ for each operator without changing their relative order. Diagonalizing the rung-Hamiltonian in this sector yields a (spin degenerate-)ground state $|3_{0(\uparrow\downarrow)}\rangle$ with energy $E_{30}$.
\[ |3_{\ell(\downarrow)}\rangle = a\left(|3'_{1\ell(\downarrow)}\rangle + |3'_{2\ell(\downarrow)}\rangle\right) + b\left(|3'_{1\ell(\downarrow)}\rangle - |3'_{2\ell(\downarrow)}\rangle\right) \\
-2a|3_{\ell(\downarrow)}\rangle \\
E_{30} = \frac{1}{2}(3\epsilon_p - t_\perp - \epsilon) \quad (A2) \]

For brevity the site index 'l' has been suppressed and
\[
a = -\frac{\sqrt{2t_{pd}^2/|12t_{pd}^2 + (\epsilon - \epsilon_p + t_\perp)^2|}}{\sqrt{12t_{pd}^2 + (\epsilon - \epsilon_p - t_\perp)^2}} \\
b = a(\epsilon - \epsilon_p + t_\perp)/(2t_{pd}) \\
\epsilon = \sqrt{12t_{pd}^2 + (\epsilon - \epsilon_p - t_\perp)^2} \quad (A3) \]

For \( \epsilon_p \approx -3eV, \ t_{pd} \approx -1eV, \) and \( t_\perp \approx 0.25eV \) one gets \( a \approx -0.16, \ b \approx 0.65, \) and \( E_{30} = -7eV \).

In the 2-particle space with no double-occupancy of the d-levels there are thirteen states, the creation operators of which we label as follows
\[
2'_{1l} = d_{1l\uparrow}^d d_{2l\downarrow}^d \\
2'_{2l} = d_{1l\downarrow}^d d_{2l\uparrow}^d \\
2'_{3l} = d_{1l\uparrow}^d d_{1l\downarrow}^d \\
2'_{4l} = d_{2l\uparrow}^d d_{2l\downarrow}^d \\
2'_{5l} = \frac{1}{\sqrt{2}}(2'_{7} - 2'_{12}) \\
2'_{6l} = \frac{1}{\sqrt{2}}(2'_{8} - 2'_{11}) \\
2'_{7l} = \frac{1}{2}(2'_{5} + 2'_{6} - 2'_{9} - 2'_{10}) \\
2'_{8l} = \frac{1}{2}(2'_{5} - 2'_{6} + 2'_{9} - 2'_{10}) \\
2'_{9l} = \frac{1}{2}(2'_{7} + 2'_{12}) \\
2'_{10l} = \frac{1}{\sqrt{2}}(2'_{8} + 2'_{11}) \\
2'_{11l} = \frac{1}{2}(2'_{5} + 2'_{6} + 2'_{9} + 2'_{10}) \\
2'_{12l} = (2'_{5} - 2'_{6} - 2'_{9} + 2'_{10} + \beta_2'2'_{13})\beta_3 \\
2'_{13l} = (2'_{5} - 2'_{6} - 2'_{9} + 2'_{10} + \gamma_2'2'_{13})\gamma_3 \quad (A4) \]

To simplify matters we will consider the high-energy states with two holes on the oxygen site as decoupled from the remaining Hilbert space. In the following these states will be discarded when evaluating the exchange integrals. With this simplification the eigenstates \( |2\mu\rangle \) are created by the following set of operators
\[
2_1 = 2'_1 \\
2_2 = 2'_2 \\
2_3 = 2'_3 \\
2_4 = 2'_4 \\
2_5 = \frac{1}{\sqrt{2}}(2_7 - 2_12) \\
2_6 = \frac{1}{\sqrt{2}}(2_8 - 2_11) \\
2_7 = \frac{1}{2}(2_5 + 2_6 - 2_9 - 2_10) \\
2_8 = \frac{1}{2}(2_5 - 2_6 + 2_9 - 2_10) \\
2_9 = \frac{1}{2}(2_7 + 2_12) \\
2_{10} = \frac{1}{\sqrt{2}}(2_8 + 2_11) \\
2_{11} = \frac{1}{2}(2_5 + 2_6 + 2_9 + 2_10) \\
2_{12} = (2_5 - 2_6 - 2_9 + 2_10 + \beta_22_13)\beta_3 \\
2_{13} = (2_5 - 2_6 - 2_9 + 2_10 + \gamma_22_13)\gamma_3 \quad (A5) \]

where, as before, the site index has been suppressed and
\[
\beta_1(\gamma_1) = \pm \epsilon_p \mp t_\perp \mp \sqrt{16t_{pd}^2 + (\epsilon_p - t_\perp)^2} \quad (A6) \\
\beta_2(\gamma_2) = 8t_{pd}/\beta_1(\gamma_1) \\
\beta_3(\gamma_3) = \beta_1(\gamma_1)/\left[8t_{pd} \sqrt{1 + \beta_1(\gamma_1)^2/16t_{pd}^2}\right] \]

with upper(lower) signs on the r.h.s of (A6) referring to \( \beta(\gamma) \). The eigenenergies are given by
\[
E_{2_{12}} = E_{20} = 2\epsilon_p - \beta_1/2 \approx -6.95eV \\
E_{2_{28}} = ... = E_{2_{28}} \approx \epsilon_p + t_\perp \approx -3.25eV \\
E_{2_{22}} = ... = E_{2_{21}} \approx \epsilon_p + t_\perp \approx -2.75eV \quad (A7) \\
E_{2_{23}} = E_{23} \approx 2\epsilon_p + 2\gamma/2 \approx -1.80eV \\
E_{2_{24}} = ... = E_{2_{24}} = 0 \]

and have been labeled into ascending order of their numerical values as relevant to NaV_{2}O_{5}.

The 3-particle space is fourfold degenerate with respect to \( H_0 \) and the eigenstates are created by
\[
4'_{1l} = d_{1l\uparrow}^{\dagger} d_{2l\uparrow} p_{t_{l\downarrow}}^\dagger p_{t_{l\downarrow}}^\dagger \\
4'_{2l} = d_{1l\downarrow}^{\dagger} d_{2l\downarrow} p_{t_{l\uparrow}}^\dagger p_{t_{l\uparrow}}^\dagger \\
4'_{3l} = d_{1l\uparrow}^{\dagger} d_{1l\downarrow}^{\dagger} p_{t_{l\uparrow}}^\dagger p_{t_{l\downarrow}}^\dagger \\
4'_{4l} = d_{2l\uparrow}^{\dagger} d_{2l\downarrow}^{\dagger} p_{t_{l\uparrow}}^\dagger p_{t_{l\downarrow}}^\dagger \quad (A8) \]

where \( E_{40} = 2\epsilon_p \).

To second order in \( H_1 \), the exchange integral \( J \) is obtained from the energy-dependent transverse spin-flip matrix-elements \( J^{-+}(z) \) and \( J^{-+}(z) \) of the corresponding second-order effective Hamiltonian
\[
\frac{1}{2}J^{-+}(z) = \langle 3_{0\ell4}3_{0\ell+1\uparrow}\rangle W \frac{1}{z - H_0} W \langle 3_{0\ell1}3_{0\ell+1\downarrow}\rangle \quad (A9) \]

where \( W \) stands for \( H_1 \) and the energy variable \( z \) is zero in the evaluation of the exchange integral. The factor \( 1/2 \) in front of \( J^{-+} \) corresponds to the fact that in \( H(H_{cis}) \)
\[
S_{l_1}^z S_{l_{l+1}}^z + S_{l_1}^z S_{l_{l+1}}^z = \frac{1}{2}(S_{l_1}^z S_{l_{l+1}}^z - S_{l_1}^z S_{l_{l+1}}^z). \\
\]

To second order the Raman scattering amplitude is obtained by considering Eq. (A9) again, however with \( W \) denoting the current operator, i.e. \( j_{3\ell}/e \), in this case and with \( z \) depending on the energy of the incoming/outgoing photon \( \omega_{in}/\omega_{out} \). Then,
\[
R^{-+}(\omega_{in},\omega_{out}) = J^{-+}(\omega_{in}) + J^{-+}(-\omega_{out}) \quad (A10) \]

The first term on the r.h.s of the previous equation describes the process where first the incoming photon is absorbed in going into the intermediate state, while the second term describes the process where the intermediate state is reached by first emitting the outgoing photon.

Equation (A9) is evaluated using first the transition amplitudes \( \langle \mu|H_1|3_{0\ell l}(\downarrow)3_{0\ell+1\downarrow}(\uparrow) \rangle \) from the 3\( \otimes \)3-particle ground states into the bare intermediate 2\( \otimes \)4-particle states \( |\mu\rangle \) as constructed from (A4) and (A8) and second by projecting the latter onto the 2\( \otimes \)4-particle eigenstates of \( H_0 \), i.e. (A5) and (A8)
\[
J^{-+}(z) = 2 \sum_{ij,\mu > 0,\nu > 0} \frac{\langle 3_{0\ell4}3_{0\ell+1\uparrow}\rangle W |\mu\rangle \langle 2_{i4}4_{j+1}\rangle}{z - (E_{2_{12}} + E_{44} - 2E_{30})} \quad (A11) \]
The preceding involves 2(4)-particle states on rungs \(l(l+1)\) only, since the hermitian-conjugate exchange path involving 4(2)-particle states on rungs \(l(l+1)\) can be accounted for by the global prefactor of 2, both, for \(W = H_1\) and \(W = j_b/e\). Moreover, since up to a factor of \((-i)\equiv 1\) the weights in the numerator of (A11) are identical for \(W = H_1\) and \(W = j_b/e\) we consider the former only. Table (A12) lists the bare intermediate states \(|\mu\rangle\) and the corresponding weights.

\[
\begin{array}{|c|c|c|c|}
\hline
\mu & |\mu\rangle & \langle \mu | H_1 | 3_{0\mu} + 3_{0\mu+1} \rangle & \langle \mu | H_1 | 3_{0\mu} + 3_{0\mu+1} \rangle \\
\hline
1 & 9 & -a^2t_{pp} & a^2t_{pp} \\
2 & 10 & -a^2t_{pp} & a^2t_{pp} \\
3 & 11 & -a^2t_{pp} & a^2t_{pp} \\
4 & 12 & -a^2t_{pp} & a^2t_{pp} \\
5 & 13 & 0 & -4a^2t_{pp} \\
6 & 14 & 0 & 4a^2t_{pp} \\
7 & 15 & a_b^t_{pp} & a_{bt}^* \\
8 & 16 & 0 & -a_b^t_{pp} \\
9 & 17 & ab(2t_{pp}^*+t_{pp}) & 0 \\
10 & 18 & -a_b^t_{pp} & 0 \\
11 & 19 & -a_b^t_{pp} & 0 \\
12 & 20 & 0 & ab(2t_{pp}^*+t_{pp}) \\
13 & 21 & 0 & 0 \\
14 & 22 & 0 & -a_b^t_{pp} \\
15 & 23 & 0 & -a_b^t_{pp} \\
16 & 24 & 0 & ab(2t_{pp}^*+t_{pp}) \\
17 & 25 & 0 & -ab(2t_{pp}^*+t_{pp}) \\
18 & 26 & ab(t_{pp}^*+2t_{pp}) & 0 \\
19 & 27 & 0 & 0 \\
20 & 28 & 0 & -a_b^t_{pp} \\
\hline
\end{array}
\]

(A12)

The constraint in (A11) on the summation over the indices \(\mu\) and \(\nu\) reflects the restriction to intermediate states with at most one \(p\)-hole. Using (A13), (A14), and (A15) it is a matter of straightforward algebra to show that

\[
J^{--}(z) = \sum_{i=1}^{4} \frac{A_i^{++}}{z - \Delta E_i}
\]

(A13)

where

\[
\Delta E_1 = E_{20} + E_{40} - 2E_{30} \approx 1.05 \text{eV}
\]

\[
\Delta E_2 = E_{21} + E_{40} - 2E_{30} \approx 4.75 \text{eV}
\]

\[
\Delta E_3 = E_{22} + E_{40} - 2E_{30} \approx 5.25 \text{eV}
\]

\[
\Delta E_4 = E_{23} + E_{40} - 2E_{30} \approx 6.20 \text{eV}
\]

and

\[
A_{1}^{++} = \frac{-b^2(8bt_{pp} + 3a\beta)t_{pp}^2}{2|16t_{pp}^2 + \beta^2(e_c - t_{pp})|}
\]

\[
\approx -0.0246eV^2 - i0.281eV\lambda + 0.803\lambda^2
\]

\[
A_{2}^{++} = 8a^2b^2t_{pp}^2
\]

\[
\approx -0.00504eV^2 - i0.0133eV\lambda - 0.0886\lambda^2
\]

\[
A_{3}^{++} = a^2b^2t_{pp}^2
\]

\[
\approx 0.000339eV^2 + i0.00388eV\lambda - 0.0111\lambda^2
\]

\[
A_{4}^{++} = \frac{b^2(8bt_{pp} + 3a\beta)t_{pp}^2}{2|16t_{pp}^2 - \gamma (e_c - t_{pp})|}
\]

\[
\approx -0.000181eV^2 - i0.00206eV\lambda + 0.00589\lambda^2
\]

Note that the ferro/antiferromagnetic signs of the amplitudes at \(\lambda = 0\) are related to the triplet/singlet character of the intermediate states. E.g., \(A_{3}^{++}\) corresponds to a matrix element where the intermediate states are given by \(2\theta, 2\tau_0, 2\tau_1\), all of which are triplets, therefore a ferromagnetic sign of \(A_{3}^{++}\) arises. Inserting the numerical values of \(A_{3}^{++}\) into (A13) we get \(J^{--}(z) \approx 0.049eV - 1.492\lambda^2/eV + i0.542\lambda\).

1. I. J. Dzyaloshinskii, J. Phys. Chem. Solids 4, 241 (1958).
2. T. Moriya, Phys. Rev. 120, 91 (1960).
3. D. Coffey, K. S. Bedell, and S. A. Trugman, Phys. Rev. B 42, 6509 (1990).
4. T. Yildirim, A. B. Harris, A. Aharony, and O. Entin-Wohlman, Phys. Rev. Lett. 89, 137202 (2002).
5. T. Yildirim, A. B. Harris, A. Aharony, and O. Entin-Wohlman, Phys. Rev. B 82, 100403(R) (2010).
6. T. Yildirim, A. B. Harris, A. Aharony, and O. Entin-Wohlman, Phys. Rev. B 82, 100403(R) (2010).
7. T. Yildirim, A. B. Harris, A. Aharony, and O. Entin-Wohlman, Phys. Rev. B 82, 100403(R) (2010).
8. T. A. Kaplan, Z. Phys. B 72, 431 (1983).
9. H. Smolinski, C. Gros, W. Weber, U. Peuchert, G. Roth, M. Weiden and C. Geibel, Phys. Rev. Lett. 80, 5164 (1998).
10. D. Sa and C. Gros, cond-mat/0004025.
11. M. Isobe, H. Sawa, K. Hamacher and W. Wenzel, preprint.
12. T. Ohama, A. Goto, T. Shimizu, E. Ninomiya, H. Sawa, M. Isobe, Y. Ueda, Sissa-cond-mat/0003141.
13. H. S. Luther, H. Nojiri, M. Motokawa, M. Isobe, and Y. Ueda, J. Phys. Soc. Jpn. 75, 3715 (1999).
14. H. S. Luther, H. Nojiri, M. Motokawa, M. Isobe, and Y. Ueda, J. Phys. Soc. Jpn. 75, 3715 (1999).
15. M. Lohmann, H.-A. Krug von Nidda, M. V. Eremin, A. Loidl, G. Obermeier, S. Horn, cond-mat/0003485.
16. M. Fischer, P. Lemmns, G. Els, G. Güntherodt, E. Sherman, E. Morre, C. Geibel and F. Steglich, Phys. Rev. B in press (in press), and P. Lemmns, private communication.
17. W. Brenig, P. Knoll, M. Mayer Physica B 237, 95 (1997).
22 H. G. von Schnering et al., Z. Kristallogr. 213, 246 (1998).
23 F. Mila, P. Millet, and J. Bonvoisin, Phys. Rev B 54, 11925 (1996).
24 P. A. Fleury and R. Loudon, Phys. Rev. 166, 514 (1968).
25 B.S. Shastry and B. Shraiman, Phys. Rev. Lett. 65, 1068 (1990); Int. J. Mod. Phys. B 5, 365 (1991).
26 V. N. Muthukumar, C. Gros, W. Wenzel, R. Valents, P. Lemmens, B. Eisener, G. Güntherodt, M. Weiden, C. Geibel, and F. Steglich, Phys. Rev. B 54, R9635 (1996).
27 R. R. P. Singh, P. Prelovsek, and B. S. Shastry, Phys. Rev. Lett. 77, 4086 (1996).
28 W. Brenig, Phys. Rev B 56, 2551 (1997).
29 P. Lemmens, M. Grove, M. Fischer, G. Güntherodt, V. N. kotov, H. Kageyama, K. Onizuka, and Y. Ueda, cond-mat/0003094 and private communication.
30 M. Hase, I. Terasaki and K. Uchinokura, Phys. Rev. Lett. 70, 3651 (1993).
31 T. Yosihama et al., J. Phys. Soc. Jap. 67, 744 (1998).
32 H. Kageyama et al, Phys. Rev. Lett. 82, 3168 (1999).
33 H. Nojiri, H. Kageyama, K. Onizuka, Y. Ueda and M. Motokawa, J Phys. Soc. Jap. 68, 2906 (1999).
34 T. Rõõm, U. Nagel, E. Lippmaa, H. Kageyama, K. Onizuka, and Y. Ueda, cond-mat/9909284.