

## Dzyaloshinskii-Moriya interaction in $\text{NaV}_2\text{O}_5$ : 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  $\text{NaV}_2\text{O}_5$ . 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.

### I. INTRODUCTION

More than four decades ago, Dzyaloshinskii<sup>1</sup> and Moriya<sup>2</sup> 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 1990s, this interaction was discussed intensively in connection with the copper-oxide compounds. In particular,  $\text{La}_2\text{CuO}_4$  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.<sup>3-5</sup> Yildirim *et al.*<sup>6</sup> 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.<sup>5-8</sup>

The DM interaction has gained renewed interest in the context of the novel transition-metal oxide  $\text{NaV}_2\text{O}_5$ , which is believed to be a quarter-filled ladder compound in its high-temperature phase.<sup>9</sup> 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.<sup>10</sup> A series of recent studies has addressed the nature of the low-temperature state.<sup>11-16</sup>

In this context it is of interest that very recent electron spin resonance (ESR) experiments<sup>17,18</sup> 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 shown no scattering intensity for  $\text{NaV}_2\text{O}_5$  (Ref. 19) which could be due to a very small cross section.

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 oxide superconductors<sup>20</sup> such

analysis is lacking. Therefore, it is the purpose of this paper to present a detailed description of the Raman operator for  $\text{NaV}_2\text{O}_5$ . In this context particular emphasis will be given to the role of the DM interaction which by symmetry is allowed in this material.

### II. HAMILTONIAN

Above the spin-charge transition temperature  $T_C$   $\text{NaV}_2\text{O}_5$  crystallizes in the centrosymmetric  $Pm\bar{m}n$  space group.<sup>9,21</sup> The compound consists of  $\text{VO}_5$  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  $\text{NaV}_2\text{O}_5$  can be thought of as consisting of ladders of V-O-V rungs along  $b$  which are weakly coupled along  $a$  (see Fig. 1).

Discarding single-ion anisotropy, a general form of any scalar two-spin interaction between consecutive rungs along

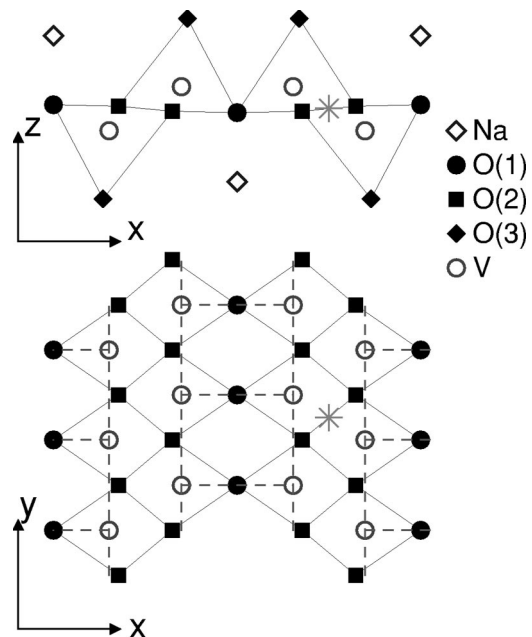


FIG. 1. Crystal structure of  $\text{NaV}_2\text{O}_5$  in the high-temperature phase. The star denotes the location of the center of inversion, the dashed lines the constituting V-O-V ladders.

the  $b$  direction of the ladder in  $\text{NaV}_2\text{O}_5$  consists of two contributions

$$H^{(S)} = JH^{(\text{Heis})} + DH^{(\text{DM})}, \quad (1)$$

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

$$H^{(\text{Heis})} = \sum_l \mathbf{S}_l \cdot \mathbf{S}_{l+1},$$

$$H^{(\text{DM})} = \sum_l \mathbf{e} \cdot (\mathbf{S}_l \times \mathbf{S}_{l+1}), \quad (2)$$

where  $\mathbf{S}_l$  denotes the total spin on rung  $l$ . The form of the Dzyaloshinskii-Moriya 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. 1).

The standard derivation of Eq. (2) for the case of magnetic moments *localized* at single ionic sites can be found in the literature,<sup>2,7,8</sup> where it is shown that both terms in this Hamiltonian can be derived from generalized exchange processes. In the present paper, however, we aim at a microscopic derivation of Eq. (2) for the case of the *mixed-valence* system  $\text{NaV}_2\text{O}_5$ . We start from a three-band Hubbard-model for  $\text{NaV}_2\text{O}_5$  in which we retain only the two active  $d$  orbitals of the V and the single O(1) site on each rung. For simplicity we consider the O(2) sites on the legs of the ladder to be integrated out, giving rise to an effective V-V hopping  $-t_{\parallel}$  along the leg. We denote by  $d_{l\alpha\sigma}^{\dagger}$  the creation operators for spin- $\sigma$  electrons in V- $d_{xy}$  orbitals on site  $\alpha$  ( $\alpha = 1, 2$ ) of the  $l$ th rung and by  $p_{l\sigma}^{\dagger}$  the creation operator of spin- $\sigma$  electrons in the O(1)- $p_y$  orbital on the  $l$ th rung. The Hamiltonian  $H = H_0 + H_1$  reads

$$H_0 = \sum_{l,\sigma} (t_{\perp} d_{l1\sigma}^{\dagger} d_{l2\sigma} + t_{dp} (d_{l1\sigma}^{\dagger} + d_{l2\sigma}^{\dagger}) p_{l\sigma} + \text{c.c.})$$

$$+ \epsilon_p \sum_{l\sigma} p_{l\sigma}^{\dagger} p_{l\sigma} + U \sum_{l\alpha} d_{l\alpha\uparrow}^{\dagger} d_{l\alpha\uparrow} d_{l\alpha\downarrow}^{\dagger} d_{l\alpha\downarrow},$$

$$H_1 = \sum_{l,\alpha\sigma} (t_{\sigma} d_{l\alpha\sigma}^{\dagger} d_{l+1\alpha\sigma} + t_{\sigma}^* d_{l+1\alpha\sigma}^{\dagger} d_{l\alpha\sigma})$$

$$- t_{pp} \sum_{l,\sigma} (p_{l\sigma}^{\dagger} p_{l+1\sigma} + p_{l+1\sigma}^{\dagger} p_{l\sigma}), \quad (3)$$

The hybridization matrix elements in Eq. (3) are (i)  $t_{\perp}$  which denotes the direct hopping of electrons between the V- $d_{xy}$  orbitals on sites 1 and 2 on a rung, (ii)  $t_{dp}$  which denotes the charge transfer integral between the V- $d_{xy}$  and O(1)- $p_y$  orbitals on a rung, (iii)  $t_{\sigma} = -t_{\parallel} + i\sigma\tilde{\lambda}$  is the hopping of electrons with spin  $\sigma = \pm 1$  between the V- $d_{xy}$  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<sup>2</sup> of strength  $\lambda$ , where  $\tilde{\lambda} \sim \lambda$ . 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 Eq. (3) have been estimated<sup>9</sup> to be  $\epsilon_p \approx -3$  eV,  $t_{\perp} \approx 0.25$  eV,  $t_{dp} \approx -1$  eV,  $t_{\parallel} \approx -0.175$  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  $U \rightarrow \infty$ , since we expect that any finite  $U$  will lead to qualitatively similar results while increasing the complexity of the calculation needlessly.<sup>22</sup>

### 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 three-particle subspace. In addition, for the calculation of the exchange matrix elements, intermediate states in the two- and four-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 the Appendix. 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. (A9). In particular,

$$J = \frac{1}{2}(J^{-+} + J^{+-}) = \text{Re}(J^{-+}). \quad (4)$$

Substituting the electronic model-parameters cited in the previous section into Eqs. (A13) and (A15) we obtain  $J \approx 0.049$  eV  $\approx 568$  K which agrees very well with the experimental value<sup>10,23</sup> of  $J_b \approx 560$  K.

Noting that  $t_{\downarrow} = t_{\uparrow}^*$  and that  $\mathbf{D} \cdot (\mathbf{S}_l \times \mathbf{S}_{l+1}) = (D/2i)(S_l^- S_{l+1}^+ - S_l^+ S_{l+1}^-)$ , we have

$$D = \frac{1}{2i}(J^{-+} - J^{+-}) = \text{Im}(J^{-+}) \quad (5)$$

for the DM coupling. Moriya<sup>2</sup> has estimated that the order of magnitude of  $D$  should be

$$D \sim (\Delta g/g)J, \quad (6)$$

where  $g$  is the gyromagnetic ratio of the Vanadium ion in octahedral crystal symmetry and  $\Delta g$  is the corresponding deviation from the free-electron value. By considering the  $g$  values obtained from ESR measurements,<sup>18</sup> we arrive at  $\Delta g/g \approx 0.01$ . Then, from Eqs. (5), (6), and (A15) where we evaluate  $D$  as a function of  $\tilde{\lambda}$ , we get an estimate for  $\tilde{\lambda}$ , i.e.,  $\tilde{\lambda} \approx 1$  meV.

#### IV. RAMAN SCATTERING

Fleury and Loudon<sup>24</sup> 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  $\text{NaV}_2\text{O}_5$  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

$$H^{(R)}(\omega_{\text{in,out}}) = J_R(\omega_{\text{in,out}})H^{(\text{Heis})} + D_R(\omega_{\text{in,out}})H^{(\text{DM})}, \quad (7)$$

where the  $\omega_{\text{in}}$  and  $\omega_{\text{out}}$  are the frequencies of the incoming and outgoing photons. The microscopic derivation  $H^{(R)}(\omega_{\text{in,out}})$  can be found in 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  $\mathbf{A} = (0, A_b, 0)$  to the current operator,<sup>25</sup> i.e.,  $H_1$  of Eq. (3) has to be replaced by  $\mathbf{j} \cdot \mathbf{A}$  with the current operator  $\mathbf{j} = (j_a, j_b, j_c)$ ,

$$j_b = ie \sum_{l,\sigma} \left( t_{pp} [P_{l\sigma}^\dagger P_{l+1\sigma} - P_{l+1\sigma}^\dagger P_{l\sigma}] \right. \\ \left. + \sum_{\alpha} [t_{\sigma} d_{l\alpha, \sigma}^\dagger d_{l+1\alpha, \sigma} - t_{\sigma}^* d_{l+1\alpha, \sigma}^\dagger d_{l\alpha, \sigma}] \right).$$

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  $J_R(\omega_{\text{in,out}})$  and  $D_R(\omega_{\text{in,out}})$  is analogous to Eq. (4) and (5)

$$J_R(\omega_{\text{in,out}}) = \text{Re}[R^{-+}(\omega_{\text{in,out}})], \\ D_R(\omega_{\text{in,out}}) = \text{Im}[R^{-+}(\omega_{\text{in,out}})]. \quad (8)$$

Note that a magnetic Raman process is possible only if  $H^{(R)}(\omega_{\text{in,out}})$  induces transitions between different eigenstates of  $H^{(S)}$ ,<sup>26–28</sup> i.e., if

$$[H^{(R)}(\omega_{\text{in,out}}), H^{(S)}] = [J_R(\omega_{\text{in,out}})D - D_R(\omega_{\text{in,out}})J] \\ \times [H^{(\text{Heis})}, H^{(\text{DM})}] \\ \neq 0. \quad (9)$$

From Eq. (9) we conclude that magnetic Raman scattering from  $\text{NaV}_2\text{O}_5$ , if modeled by Eq. (3), arises because two conditions are simultaneously satisfied. First, the existence of a spin-orbit coupling leads to a nonvanishing commutator in Eq. (9). Second, because the number of available paths for the magnetic and the photon induced exchange is larger than one *and* because  $\omega_{\text{in,out}} \neq 0$  the factor of  $J_R(\omega_{\text{in,out}})D - D_R(\omega_{\text{in,out}})J$  is nonzero. The latter is true despite the formal similarity between the Raman scattering amplitude and the magnetic exchange integral, because  $H^{(R)}(\omega_{\text{in,out}})$  displays an additional dependence on the photon energies. More specifically, for a *single* exchange path  $J_R(\omega_{\text{in,out}})D$

$-D_R(\omega_{\text{in,out}})J = 0$  for any value of  $\omega_{\text{in,out}}$  while for more than one exchange path  $J_R(\omega_{\text{in,out}})D - D_R(\omega_{\text{in,out}})J$  vanishes only at  $\omega_{\text{in,out}} = 0$ .

Next, we would like to point out that from the two terms,  $H^{(\text{Heis})}$  and  $H^{(\text{DM})}$  which make up  $H^{(R)}(\omega_{\text{in,out}})$  it is actually  $H^{(\text{DM})}$  which drives the magnetic Raman process. Up to now we have only considered anisotropic contributions to  $H^{(S)}$  to leading order in  $\tilde{\lambda}$ . Kaplan<sup>8</sup> and Shekhtman *et al.*<sup>7</sup> have shown that, in general, the next-order term  $H^{(\text{KSAE})} \sim \sum_l (\mathbf{e} \cdot \mathbf{S}_l) (\mathbf{e} \cdot \mathbf{S}_{l+1})$  contributes to the spin Hamiltonian with a very specific prefactor

$$H^{(S)} = JH^{(\text{Heis})} + DH^{(\text{DM})} + (\sqrt{J^2 - D^2} - J)H^{(\text{KSAE})}. \quad (10)$$

Starting from the model in Eq. (3) a derivation analogous to that in Refs. 7,8 can be performed giving rise to the same prefactor as in Eq. (10). Using this, it is then possible to transform  $H^{(S)}$  into an equivalent Hamiltonian of the plain Heisenberg form by means of the unitary mapping

$$\tilde{S}_l^x = \cos \varphi_l S_l^x - \sin \varphi_l S_l^y, \\ \tilde{S}_l^y = -\sin \varphi_l S_l^x + \cos \varphi_l S_l^y \quad (11)$$

with  $\tilde{S}_l^z = S_l^z$ ,  $\varphi_l = 2l\varphi_0$ , and  $\tan(2\varphi_0) = D/J$ . Expressed in terms of  $\tilde{\mathbf{S}}_l$  the Hamiltonian reads  $\tilde{H}^{(S)} = \sqrt{J^2 + D^2} \sum_l \tilde{\mathbf{S}}_l \cdot \tilde{\mathbf{S}}_{l+1}$ . Now, we note that higher order terms in  $\tilde{\lambda}$  will also contribute to the Raman operator. However, following the discussion after Eq. (9) it is obvious that Eq. (11) will not simultaneously reduce  $H^{(S)}$  and  $H^{(R)}(\omega_{\text{in,out}})$  to a canonical Heisenberg form. Therefore, in the new basis, the Raman operator takes on the form  $\tilde{H}^{(R)}(\omega_{\text{in,out}}) = \tilde{J}_R(\omega_{\text{in,out}})\tilde{H}^{(\text{Heis})} + \tilde{D}_R(\omega_{\text{in,out}})\tilde{H}^{(\text{DM})} + O(\tilde{\lambda}^2)$ . The only part of  $\tilde{H}^{(R)}(\omega_{\text{in,out}})$  which does not commute with  $\tilde{H}^{(S)}$  to lowest order in  $\tilde{\lambda}$  is the DM interaction, i.e.,  $\tilde{H}^{(R)}(\omega_{\text{in,out}}) \equiv \tilde{D}_R(\omega_{\text{in,out}})\tilde{H}^{(\text{DM})}$ .

This completes our derivation of the Raman operator for the *homogeneous* phase of  $\text{NaV}_2\text{O}_5$  as realized for  $T > T_C$ . Quite generally the preceding demonstrates that a DM contribution to the Raman operator  $H^{(R)}(\omega_{\text{in,out}})$  will occur in multiband systems whenever a DM exchange interaction is allowed locally. Obviously it is tempting to analyze the effects of this form of  $H^{(R)}(\omega_{\text{in,out}})$  also on a *dimerized* spin-liquid state, as present in  $\text{NaV}_2\text{O}_5$  for  $T < T_C$  and similarly in  $\text{CuGeO}_3$  for  $T < T_{\text{SP}}$ .<sup>29</sup> To this end let  $H^{(R)}(\omega_{\text{in,out}})$  act on a pure dimer state  $|\Phi_0\rangle = |s_1 \cdots s_\mu \cdots\rangle$ , where  $\mu$  labels nearest-neighbor pairs of spins which are in a relative singlet state  $|s_\mu\rangle$ —for the case of  $\text{NaV}_2\text{O}_5$  these pairs of spins correspond to pairs of rungs  $(2l, 2l+1)$ . One obtains

$$H^{(\text{DM})}|\Phi_0\rangle = \sum_{\mu} (-2i |\cdots t_{\mu}^z \cdots\rangle - |\cdots t_{\mu}^x t_{\mu+1}^y \cdots\rangle \\ + |\cdots t_{\mu}^y t_{\mu+1}^x \cdots\rangle). \quad (12)$$

Here  $|t_{\mu}^{\alpha}\rangle$  ( $\alpha = x, y, z$ ) refers to triplet states on the dimer bonds. While the second and third term on the right-hand side of Eq. (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  $\mathbf{e}$  (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<sup>17,18</sup> which probe the existence of a DM interaction in  $\text{NaV}_2\text{O}_5$ , 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  $\text{NaV}_2\text{O}_5$  and, additionally, have discussed its effect in the dimerized state.

In the dimerized state two Raman modes have been observed in  $\text{NaV}_2\text{O}_5$  in  $bb$  polarization at 66 and 104  $\text{cm}^{-1}$ . Tentatively these modes have been ascribed to magnetic bound states of total-spin zero.<sup>19</sup> 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.<sup>11,30</sup> 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 processes [see Eq. (12)].

Clear evidence for a DM vector in  $\text{NaV}_2\text{O}_5$  along the  $z$  direction has been provided by ESR experiments.<sup>18</sup> While these authors have interpreted their findings in terms of quasistatic 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 nontrivial DM contribution to the magnetic Raman process whenever at least two *nonequivalent* 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  $\text{NaV}_2\text{O}_5$  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  $\text{SrCu}_2(\text{BO}_3)_2$  (Ref. 31) have been found by ESR (Ref. 32) and far-infrared spectroscopy.<sup>33</sup> Therefore one might speculate if one-magnon Raman modes with the special signature described in the previous section could be observable in  $\text{SrCu}_2(\text{BO}_3)_2$ .

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## APPENDIX: EXCHANGE INTEGRAL AND RAMAN AMPLITUDE

In this appendix we present details of the evaluation of the two, three, and four-particle eigenstates on a rung as well as the matrix elements relevant to the exchange integral and the Raman operator. We begin with the three-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

$$\begin{aligned} 3'_{1\uparrow} &= d_{1\uparrow}^\dagger d_{2\downarrow}^\dagger p_{l\uparrow}^\dagger, & 3'_{2\uparrow} &= d_{1\downarrow}^\dagger d_{2\uparrow}^\dagger p_{l\uparrow}^\dagger, \\ 3'_{3\uparrow} &= d_{2\uparrow}^\dagger p_{l\uparrow}^\dagger p_{l\downarrow}^\dagger, & 3'_{4\uparrow} &= d_{1\uparrow}^\dagger p_{l\uparrow}^\dagger p_{l\downarrow}^\dagger, \\ 3'_{5\uparrow} &= d_{1\uparrow}^\dagger d_{2\uparrow}^\dagger p_{l\downarrow}^\dagger. \end{aligned} \quad (\text{A1})$$

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  $E_{30}$

$$\begin{aligned} |3_{0\uparrow(\downarrow)}\rangle &= a(|3'_{1\uparrow(\downarrow)}\rangle + |3'_{2\uparrow(\downarrow)}\rangle) \\ &+ b[|3'_{4\uparrow(\downarrow)}\rangle - |3'_{3\uparrow(\downarrow)}\rangle] - 2a|3'_{5\uparrow(\downarrow)}\rangle, \\ E_{30} &= \frac{1}{2}(3\epsilon_p - t_\perp - \epsilon). \end{aligned} \quad (\text{A2})$$

For brevity the site index  $l'$  has been suppressed and

$$\begin{aligned} a &= -\sqrt{2t_{pd}^2/[12t_{pd}^2 + (\epsilon - \epsilon_p + t_\perp)^2]}, \\ b &= a(\epsilon - \epsilon_p + t_\perp)/(2t_{pd}), \\ \epsilon &= \sqrt{12t_{pd}^2 + (\epsilon_p - t_\perp)^2}. \end{aligned} \quad (\text{A3})$$

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

In the two-particle space with no double occupancy of the  $d$  levels there are thirteen states, the creation operators of which we label

$$\begin{aligned} 2'_{1l} &= d_{1\uparrow}^\dagger d_{2\downarrow}^\dagger, & 2'_{2l} &= d_{1\downarrow}^\dagger d_{2\uparrow}^\dagger, & 2'_{3l} &= d_{1\downarrow}^\dagger d_{2\downarrow}^\dagger, \\ 2'_{4l} &= d_{1\uparrow}^\dagger d_{2\uparrow}^\dagger, & 2'_{5l} &= d_{1\downarrow}^\dagger p_{l\uparrow}^\dagger, & 2'_{6l} &= d_{1\uparrow}^\dagger p_{l\downarrow}^\dagger, \\ 2'_{7l} &= d_{1\uparrow}^\dagger p_{l\uparrow}^\dagger, & 2'_{8l} &= d_{1\downarrow}^\dagger p_{l\downarrow}^\dagger, & 2'_{9l} &= d_{2\uparrow}^\dagger p_{l\downarrow}^\dagger, \\ 2'_{10l} &= d_{2\downarrow}^\dagger p_{l\uparrow}^\dagger, & 2'_{11l} &= d_{2\downarrow}^\dagger p_{l\downarrow}^\dagger, & 2'_{12l} &= d_{2\uparrow}^\dagger p_{l\uparrow}^\dagger, \\ 2'_{13l} &= p_{l\uparrow}^\dagger p_{l\downarrow}^\dagger. \end{aligned} \quad (\text{A4})$$

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  $|2_{ii}\rangle$  are created by the following set of operators:

$$2_1 = 2'_{1l},$$



$$\begin{aligned}
2_2 &= 2'_2, & 4'_{1l} &= d_{1l\uparrow}^\dagger d_{2l\uparrow}^\dagger p_{l\uparrow}^\dagger p_{l\downarrow}^\dagger, & 4'_{2l} &= d_{1l\downarrow}^\dagger d_{2l\uparrow}^\dagger p_{l\uparrow}^\dagger p_{l\downarrow}^\dagger, & (A8) \\
2_3 &= 2'_3, & & & & & \\
2_4 &= 2'_4, & 4'_{3l} &= d_{1l\uparrow}^\dagger d_{2l\downarrow}^\dagger p_{l\uparrow}^\dagger p_{l\downarrow}^\dagger, & 4'_{4l} &= d_{1l\downarrow}^\dagger d_{2l\downarrow}^\dagger p_{l\uparrow}^\dagger p_{l\downarrow}^\dagger, & 
\end{aligned}$$

$$2_5 = \frac{1}{\sqrt{2}}(2'_7 - 2'_{12}),$$

$$2_6 = \frac{1}{\sqrt{2}}(2'_8 - 2'_{11}),$$

$$2_7 = \frac{1}{2}(2'_5 + 2'_6 - 2'_9 - 2'_{10}),$$

$$2_8 = \frac{1}{2}(2'_5 - 2'_6 + 2'_9 - 2'_{10}),$$

$$2_9 = \frac{1}{\sqrt{2}}(2'_7 + 2'_{12}),$$

$$2_{10} = \frac{1}{\sqrt{2}}(2'_8 + 2'_{11}),$$

$$2_{11} = \frac{1}{2}(2'_5 + 2'_6 + 2'_9 + 2'_{10}),$$

$$2_{12} = (2'_5 - 2'_6 - 2'_9 + 2'_{10} + \beta_2 2'_{13}) \beta_3,$$

$$2_{13} = (2'_6 - 2'_5 - 2'_{10} + 2'_9 + \gamma_2 2'_{13}) \gamma_3, \quad (A5)$$

where, as before, the site index has been suppressed and

$$\beta_1(\gamma_1) = \pm \epsilon_p \mp t_\perp + \sqrt{16t_{pd}^2 + (\epsilon_p - t_\perp)^2}, \quad (A6)$$

$$\beta_2(\gamma_2) = 8t_{pd} / \beta_1(\gamma_1),$$

$$\beta_3(\gamma_3) = \beta_1(\gamma_1) \left/ \left[ 8t_{pd} \sqrt{1 + \frac{\beta_1(\gamma_1)^2}{16t_{pd}^2}} \right] \right.$$

with upper (lower) signs on the right-hand side of Eq. (A6) referring to  $\beta$  ( $\gamma$ ). The eigenenergies are given by

$$E_{2_{12}} \equiv E_{20} = 2\epsilon_p - \beta_1/2 \approx -6.95 \text{ eV},$$

$$E_{2_5} = \dots = E_{2_8} \equiv E_{21} = \epsilon_p - t_\perp \approx -3.25 \text{ eV},$$

$$E_{2_9} = \dots = E_{2_{11}} \equiv E_{22} = \epsilon_p + t_\perp \approx -2.75 \text{ eV}, \quad (A7)$$

$$E_{2_{13}} = E_{23} \equiv E_{24} = \epsilon_p + \gamma_1/2 \approx -1.80 \text{ eV},$$

$$E_{2_1} = \dots = E_{2_4} \equiv E_{24} = 0,$$

and have been labeled into ascending order of their numerical values as relevant to  $\text{NaV}_2\text{O}_5$ .

The three-particle space is fourfold degenerate with respect to  $H_0$  and the eigenstates are created by

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

$$\frac{1}{2}J^{-+}(z) \equiv \left\langle 3_{0l\downarrow} 3_{0l+1\uparrow} \left| W \frac{1}{z - H_0} W \right| 3_{0l\uparrow} 3_{0l+1\downarrow} \right\rangle, \quad (A9)$$

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  $H^{\text{(Heis)}}$   $S_l^x S_{l+1}^x + S_l^y S_{l+1}^y = \frac{1}{2}(S_l^+ S_{l+1}^- + S_l^- S_{l+1}^+)$ .

To second order the Raman scattering amplitude is obtained by considering Eq. (A9) again, however, with  $W$  denoting the current operator, i.e.,  $j_b/e$ , in this case and with  $z$  depending on the energy of the incoming/outgoing photon  $\omega_{\text{in}}/\omega_{\text{out}}$ . Then,

$$R^{-+}(\omega_{\text{in}}, \omega_{\text{out}}) = J^{-+}(\omega_{\text{in}}) + J^{-+}(-\omega_{\text{out}}). \quad (A10)$$

The first term on the right-hand side 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  $\langle \mu | H_1 | 3_{0l\uparrow(\downarrow)} 3_{0l+1\downarrow(\uparrow)} \rangle$  from the  $3 \otimes 3$ -particle ground states into the bare intermediate  $2 \otimes 4$ -particle states  $|\mu\rangle$  as constructed from Eq. (A4) and (A8) and second by projecting the latter onto the  $2 \otimes 4$ -particle eigenstates of  $H_0$ , i.e., Eqs. (A5) and (A8)

$$\begin{aligned}
J^{-+}(z) &= 2 \sum_{ij, \mu > 6, \nu > 6} \left[ \langle 3_{0l\downarrow} 3_{0l+1\uparrow} | W | \mu \rangle \langle \mu | 2_{il} 4_{jl+1} \rangle \right. \\
&\quad \left. \times \frac{\langle 2_{il} 4_{jl+1} | \nu \rangle \langle \nu | W | 3_{0l\uparrow} 3_{0l+1\downarrow} \rangle}{z - (E_{2_i} + E_{4_j} - 2E_{30})} \right]. \quad (A11)
\end{aligned}$$

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  $(-i)i \equiv 1$  the weights in the numerator of Eq. (A11) are identical for  $W = H_1$  and  $W = j_b/e$  we consider the former only. Equation (A12) lists the bare intermediate states  $|\mu\rangle$  and the corresponding weights.

$\mu$	$\mu$	$\langle \mu   H_1   3_{0\downarrow} 3_{0\downarrow+1\uparrow} \rangle$	$\langle \mu   H_1   3_{0\downarrow} 3_{0\downarrow+1\uparrow} \rangle$
1	$ 2'_{1l} 4'_{3l+1}\rangle$	$-a^2 t_{pp}$	$a^2 t_{pp}$
2	$ 2'_{2l} 4'_{3l+1}\rangle$	$-a^2 t_{pp}$	$a^2 t_{pp}$
3	$ 2'_{2l} 4'_{2l+1}\rangle$	$-a^2 t_{pp}$	$a^2 t_{pp}$
4	$ 2'_{1l} 4'_{2l+1}\rangle$	$-a^2 t_{pp}$	$a^2 t_{pp}$
5	$ 2'_{3l} 4'_{1l+1}\rangle$	0	$-4a^2 t_{pp}$
6	$ 2'_{4l} 4'_{4l+1}\rangle$	$4a^2 t_{pp}$	0
7	$ 2'_{6l} 4'_{3l+1}\rangle$	$abt_{pp}$	$abt_{\downarrow}^*$
8	$ 2'_{5l} 4'_{3l+1}\rangle$	0	$-ab(2t_{\downarrow}^* + t_{pp})$
9	$ 2'_{6l} 4'_{2l+1}\rangle$	$ab(2t_{\uparrow}^* + t_{pp})$	0
10	$ 2'_{5l} 4'_{2l+1}\rangle$	$-abt_{\uparrow}^*$	$-abt_{pp}$
11	$ 2'_{7l} 4'_{4l+1}\rangle$	$-ab(t_{\downarrow}^* + 2t_{pp})$	0
12	$ 2'_{8l} 4'_{1l+1}\rangle$	0	$ab(t_{\uparrow}^* + 2t_{pp})$
13	$ 2'_{10l} 4'_{3l+1}\rangle$	$+abt_{\uparrow}^*$	$abt_{pp}$
14	$ 2'_{9l} 4'_{3l+1}\rangle$	$-ab(2t_{\uparrow}^* + t_{pp})$	0
15	$ 2'_{9l} 4'_{2l+1}\rangle$	$-abt_{pp}$	$-abt_{\downarrow}^*$
16	$ 2'_{10l} 4'_{2l+1}\rangle$	0	$ab(2t_{\downarrow}^* + t_{pp})$
17	$ 2'_{11l} 4'_{1l+1}\rangle$	0	$-ab(t_{\uparrow}^* + 2t_{pp})$
18	$ 2'_{12l} 4'_{4l+1}\rangle$	$ab(t_{\downarrow}^* + 2t_{pp})$	0
19	$ 2'_{13l} 4'_{3l+1}\rangle$	$b^2 t_{\uparrow}^*$	$-b^2 t_{\downarrow}^*$
20	$ 2'_{12l} 4'_{sl+1}\rangle$	$-b^2 t_{\uparrow}^*$	$b^2 t_{\downarrow}^*$

(A12)

The constraint in Eq. (A11) on the summation over the indices  $\mu$  and  $\nu$  reflects the restriction to intermediate states with at most one  $p$  hole. Using Eqs. (A5), (A7), and (A12) it is a matter of straightforward algebra to show that

$$J^{-+}(z) = \sum_{i=1}^4 \frac{A_i^{-+}}{z - \Delta E_i}, \quad (\text{A13})$$

where

$$\Delta E_1 = E_{20} + E_{40} - 2E_{30} \approx 1.05 \text{ eV}, \quad (\text{A14})$$

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

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

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

and

$$A_1^{-+} = -\frac{b^2(8bt_{pd} + 3a\beta_1)^2 t_{\uparrow}^{*2}}{2[16t_{pd}^2 + \beta_1(\epsilon_p - t_{\perp})]} \approx -0.0246 \text{ eV}^2 - i0.281 \text{ eV}\tilde{\lambda} + 0.803\tilde{\lambda}^2, \quad (\text{A15})$$

$$A_2^{-+} = 8a^2 b^2 t_{\uparrow}^*(t_{\uparrow}^* + t_{pp}) \approx -0.00504 \text{ eV}^2 - i0.0133 \text{ eV}\tilde{\lambda} - 0.0886\tilde{\lambda}^2,$$

$$A_3^{-+} = a^2 b^2 t_{\uparrow}^{*2} \approx 0.000339 \text{ eV}^2 + i0.00388 \text{ eV}\tilde{\lambda} - 0.0111\tilde{\lambda}^2,$$

$$A_4^{-+} = \frac{b^2(8bt_{pd} - 3a\gamma_1)^2 t_{\uparrow}^{*2}}{2[16t_{pd}^2 - \gamma_1(\epsilon_p - t_{\perp})]} \approx -0.000181 \text{ eV}^2 - i0.00206 \text{ eV}\tilde{\lambda} + 0.00589\tilde{\lambda}^2.$$

Note that the ferromagnetic and antiferromagnetic signs of the amplitudes at  $\tilde{\lambda}=0$  are related to the triplet and singlet character of the intermediate states. For example,  $A_3^{-+}$  corresponds to a matrix element where the intermediate states are given by  $2_9, 2_{10}, 2_{11}$ , all of which are triplets, therefore a ferromagnetic sign of  $A_3^{-+}$  arises. Inserting the numerical values of  $A_i^{-+}$  into Eq. (A13) we get  $J^{-+}(z=0) \approx 0.049 \text{ eV} - 1.492\tilde{\lambda}^2/\text{eV} + i0.542\tilde{\lambda}$ .

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