The Spin-SAF transition in NaV$_2$O$_5$ induced by spin-pseudospin coupling

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We present microscopic estimates for the spin-spin and spin-pseudospin interactions of the quarter-filled ladder compound NaV$_2$O$_5$, obtained by exactly diagonalizing appropriate clusters of the underlying generalized Hubbard Hamiltonian. We present evidence for a substantial interladder spin-pseudospin interaction term which would allow simultaneously for the superantiferroelectric (SAF) charge (pseudospin) ordering and spin dimerization. We discuss the values of the coupling constants appropriate for NaV$_2$O$_5$ and deduce the absence of a soft antiferroelectric mode.

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**Introduction**

The insulating transition-metal compound NaV$_2$O$_5$ is, until now, the only known quarter-filled symmetric ladder compound [4], the closely related LiV$_2$O$_5$ has asymmetric ladders [2]. It has a single electron per rung which is located in the intra-rung $V^{4.5}-V^{4.5}$ bonding orbital, forming spin-1/2 Heisenberg chains in the high-temperature state [3]. NaV$_2$O$_5$ has a dual phase transition at $T_c = 34$ K. Below this temperature two things happen: A spin gap opens [3], like in a spin-Peierls system and a crystallographic lattice distortion occurs which leads to a charge disproportionation $V^{4.5}_c-V^{4.5}_u$ on the rungs, alternating along the ladder direction [3]. Note also that in the literature on NaV$_2$O$_5$ its charge order is called the “zig-zag phase”, what characterizes the antiferroelectric order in a single ladder only. In fact, the two-dimensional long-range charge order in NaV$_2$O$_5$ is the super-antiferroelectric (SAF) [11], and we proposed to call the transition in NaV$_2$O$_5$ the spin-SAF transition. To develop an understanding of this fascinating phase transition is an important matter, as it may serve as a model for other systems with coupled spin and orbital degrees of freedom [9].

Basing ourselves on the earlier suggestion of Mostovoy and Khomskii [3] that a bilinear coupling between the charge and spin degrees of freedom, similar to the spin-phonon coupling in spin-Peierls systems, may be responsible for the transition in NaV$_2$O$_5$, we have proposed the theory of the spin-SAF transition in the coupled spin-pseudospin model [10, 11, 12], which we believe can explain the situation in that compound. In our theory the simultaneous appearance of the SAF charge order and of spin dimerization is driven by a single interladder spin-pseudospin coupling. Here we present results from a microscopic study for the strength of the coupling parameters necessary to understand the spin-SAF phase transition in NaV$_2$O$_5$.

**Microscopic Hamiltonian**

The quarter-filled ladder compound NaV$_2$O$_5$ is described microscopically by a generalized Hubbard model [12] with hopping matrix-elements $t_a$ and $t_b$ across the rung of the ladder (the crystallographic a-direction) and along the leg of the ladder respectively (the b-direction), compare Fig. 1 in addition to an interladder hopping matrix element $t_1$. The Coulomb interaction between the electrons gives rise to the on-site repulsion $U$, and the intraladder n.n. matrix elements $V_a$ (rung) and $V_b$ (leg). Here we neglect the possible intraladder diagonal repulsion $V_d$ and further interladder matrix elements.

**Pseudospin Hamiltonian**

NaV$_2$O$_5$ is an insulator and the low-energy excitations of the microscopic generalized Hubbard model can therefore be mapped in perturbation theory [3, 13], for small $t_b/U$ and small $t_b/V_a$, to a spin-pseudospin Hamiltonian. Here we consider it in the form

$$H = H_T + H_S + H_{ST},$$

with

$$H_T = 2t_a \sum_{n,m} T_n^x m_n + \frac{1}{2} g \sum_{m,n} T_n^z m_n T_{n+1,m}^z$$

$$H_S = J_1 \sum_{n,m} S_n \cdot S_{n+1,m}$$

$$H_{ST} = \varepsilon \sum_{n,m} S_n \cdot S_{n+1,m} (T_n^z m_{n+1} - T_{n+1,m}^z)$$

where the spin/pseudospin operators obey the usual spin-algebra, e.g. $[T^\alpha, T^\beta] = i\varepsilon_{\alpha\beta\gamma} T^\gamma$. The sites indices $(n, m)$ count rungs/ladders. In the high-temperature phase of NaV$_2$O$_5$ the electrons are delocalised on the...

**FIG. 1:** The clusters used for the exact-diagonalization study. (a) A 2x4 ladder with four electrons with are dominantly located on the V-V bonding orbital, indicated symbolically by the dashed ellipses. (b) A six-site cluster with two rungs and two sites of the respective adjacent ladders, with four electrons. (c) Same as (b) but with two electrons.
rungs with \( \langle T^z_{n,m} \rangle \approx -1/2 \). In the low-temperature phase a finite-degree of charge ordering occurs with \( \langle T^z_{n,m} \rangle \propto (-1)^n \).

In Fig. (3) we have neglected further intraladder spin-orbital coupling terms which are not critically relevant for the physics of the spin-SAF phase transition in \( \text{NaV}_2\text{O}_5 \) [13, 11]. The magnitude of the spin-pseudospin coupling term \( \varepsilon \) in [3] has not yet been estimated in perturbation theory, it is \( \sim t_b t_2 \).

Recently we have shown [10], that the spin- pseudospin coupling term \( H_{ST} \propto \varepsilon \) could at the same time drive the observed phase transition in \( \text{NaV}_2\text{O}_5 \) and lead to the observed opening of a gap in the spin-excitation spectrum via an alternation of the effective spin-spin coupling

\[
J_{n,m}^{\text{eff}} = J_1 + \varepsilon \langle T^z_{n,m+1} - T^z_{n,m-1} \rangle \tag{4}
\]

along the ladder.

**Spin-pseudospin coupling**—The exchange coupling \( J_1 \) in (2) can be estimated by diagonalizing small clusters of \( H \) and comparing the energy splitting between the ground-state singlet and the first excited triplet with the corresponding energy gap of the respective finite-size spin model.

The inter-ladder spin-pseudospin coupling \( \varepsilon \) can be determined using (4): First we calculate the singlet-triplet energy gaps \( \Delta E_1(N) \) of the six-site clusters illustrated in Fig. (4) (b) and (c) respectively, i.e. with \( N = 4, 2 \) electrons. The position of the spins inside the clusters shown in Fig. (4) illustrate typical spin-configurations realized for the parameters relevant for \( \text{NaV}_2\text{O}_5 \). \( \Delta E_1(N) \) therefore correspond to the triplet-energy gaps of a system \( J_1^{\text{eff}} \mathbf{S}_1 \cdot \mathbf{S}_2 \) with two spins \( \mathbf{S}_1 \) and \( \mathbf{S}_2 \) located on two n.n. rungs of the ladder, which is just \( J_1^{\text{eff}} \). For the six-site cluster with \( N = 4, 2 \) electrons we have approximatively

\[
\langle T^z_{n,m+1} - T^z_{n,m-1} \rangle \approx \begin{cases} 
1 & \text{ } \text{ } \text{ } \text{ } \text{ } \text{ } \text{ } N = 2 \\
-1 & \text{ } \text{ } \text{ } \text{ } \text{ } \text{ } \text{ } N = 4 
\end{cases}
\]

Using (4) we then find

\[
\varepsilon = (\Delta E_1(2) - \Delta E_1(4))/2 \tag{5}
\]

for the spin-pseudospin coupling \( \varepsilon \). The results are presented in Fig. (2).

**Parameters for \( \text{NaV}_2\text{O}_5 \)**—The Coulomb repulsion \( U \) has been estimated [12, 14] to be \( U \approx (3 - 4.1) \text{eV} \) for \( \text{NaV}_2\text{O}_5 \). Its exact value is not critical and we use here \( U = 3.0 \text{eV} \), all units throughout this paper are in eV. We use \( t_a = 0.35 \text{eV} \) for the intra-rung hopping \( t_a \), close to the LDA-estimate [2, 12] of 0.38 eV. The inter-rung hopping \( t_b \) along the leg of the ladder is [12, 14] approximately 0.15 eV – 0.175 eV.

The absolute magnitude of the interladder hopping matrix element \( t_1 \) has been difficult to determine from first principles. It is relatively small [2, 12, 13, 17] with a magnitude up to the estimated total interladder coupling of the order 0.06 eV. Additionally, one has attributed the smallness of the frustrating inter-ladder spin-spin coupling in the high-temperature state [2, 13, 15] to a mutual cancellation of antiferromagnetic and ferromagnetic contributions due to intermediate singlet and triplet states [13, 17]. The substantial size of \( \varepsilon \) found in our study and presented in Fig. (2) is then in qualitative agreement with the finding of Yaresko et al. of a substantial ferromagnetic interladder spin-spin coupling, within a spin-resolved density-functional study of the fully charge-ordered state [14]. We note that the true amount of charge disproportionation \( \langle T^z_{n,m+1} - T^z_{n,m-1} \rangle \) in \( \text{NaV}_2\text{O}_5 \) will be substantially reduced from unity and with a corresponding reduction of the size of the intraladder dimerization via [11].

The size of the inter-size Coulomb repulsion matrix elements \( V_a \) and \( V_b \) have been estimated to be up to half an eV [13], with a reduction from the respective bare values due to screening. The Ising-like pseudospin coupling-
FIG. 4: The frustration parameter \( \alpha = J_2/J_1 \) for the n.n./n.n.n. couplings \( J_1 \) and \( J_2 \) along the ladder, estimated by comparing \( \Delta_0/\Delta_t \) for the 4-site Heisenberg ladder (see Fig. 3) with the results obtained for the \( 2 \times 4 \) ladder (see Fig. 1(a)) for \( U = 3 \), \( t_a = 0.35 \) and various \( V_a \) and \( V_b \). For Na\( \text{V}_2\text{O}_5 \) the hopping \( t_b \) along the leg is about \( t_b \approx 0.175 \).

constant \( g \) in [11] is given by \( g = 4(V_b - V_d) \), where \( V_d \) the diagonal Coulomb repulsion matrix element in between two rungs [13]. Due to geometry we have roughly \( V_a \approx V_b \approx \sqrt{2}V_d \). In order to avoid a proliferation of parameters we have set here \( V_d = 0 \) and examined two cases, see Fig. 2: \( V_b = V_a \) and \( V_b = V_a/3 \). The latter case simulates the reduction of \( g \approx 4(V_b - V_b/\sqrt{2}) \approx 4V_a/3 \) by \( V_b \).

Intraladder frustration—Vojta et al. [17] have studied recently the possibility of a intraladder spin gap formation for extended quarter dimer Hubbard models on a single two-leg ladder, similar to the one studied here. They find a spontaneous spin gap[d] formation by DMRG for \( t_b > t_a \). This value for \( t_b \) is outside of the parameter range relevant for Na\( \text{V}_2\text{O}_5 \) but of general interest.

Here we present a novel method to analyze finite-size data which allows to obtain directly the microscopic frustration parameter \( \alpha = J_2/J_1 \), where \( J_2 \) is the n.n.n. spin-coupling.

The frustrated spin-1/2 Heisenberg chain spontaneously dimerizes for \( \alpha > \alpha_c \) and the critical \( \alpha_c \approx 0.24 \) can be accurately determined by the crossing of the singlet excitation gap \( \Delta E_s(L) \) with the triplet excitation gap \( \Delta E_t(L) \) in chains with length \( L \). For \( \alpha < \alpha_c \) we have \( \Delta E_t(L) < \Delta E_s(L) \), for \( \alpha > \alpha_c \) the other way around.

In Fig. 3 we plot the ratio \( \Delta E_s(L)/\Delta E_t(L) \) for some small Heisenberg chains of length \( L = 4, 8, 12 \), as a function of \( J_2/J_1 \). The Majumdar-Gosh state is exactly realized for \( \alpha = 0.5 \). For \( L = 4 \) there are only half as many \( J_2 \)-bonds than \( J_1 \)-bonds and the Majumdar-Gosh state is realized for \( J_2 = J_1 \), we have therefore plotted the data in Fig. 3 for \( L = 4 \) as a function of \( (J_2/J_1) \).

The finite-size scaling properties of \( \Delta E_s(L)/\Delta E_t(L) \) are here, however, unimportant. Here we point out that the ratio \( \Delta E_s(L)/\Delta E_t(L) \) is characteristic for a given \( L \).

By calculating this ratio for the four-run quarter-filled ladder illustrated in Fig. 1 we can therefore accurately determine the degree of intraladder frustration. The results are presented in Fig. 1. We confirm that the system spontaneously dimerizes for \( t_b = t_a = 0.35 \), for the parameters \( V_a = V_b \) considered by Vojta et al. [17]. We also find a tendency towards an anti-frustration, i.e. a ferromagnetic \( J_2 \) for intermediate values of \( J_2 \), indicating the absence of frustration for Na\( \text{V}_2\text{O}_5 \). In the limit \( V_a = 0 = V_b \) we find a very large and negative \( J_2 \) indicating long-range interactions. Here the analysis breaks down, as it is valid only for small to moderate values of \( J_2 \).

Finally we present in Fig. 5 our estimates for the n.n. intraladder spin coupling \( J_1 \), obtained by comparing the triplet-gap of the four-run ladder (see Fig. 1) with that of the four-site Heisenberg chain. For \( t_b = 0.15 - 0.17 \), the range relevant for Na\( \text{V}_2\text{O}_5 \) we find very reasonable value \( J_1 = 0.04 - 0.06 \), close to the experimental value \( 0.560 \text{ K} = 0.048 \text{ eV} \), which are far more accurate than those by simple perturbation theory [12].

Critical temperature—From the theory of the spin-SAF transition in the coupled spin-pseudospin model [10, 15] we obtain the following equation for the critical temperature at the Ising couplings \( g < g_c \) (i.e., at the couplings where the pure transverse Ising model [4] is always disordered)

\[
\eta(T_c/J_1) = J_1(g - g_c)/4\varepsilon^2, \tag{6}
\]

where \( \eta(x) \) is the dimerization susceptibility of the dimerized Heisenberg XXX chain with the Hamiltonian \( H_{xxx} = \sum_n J_1(1 + (-1)^n)S_nS_{n+1} \) in the limit \( \Delta \to 0 \), and \( g_c = 4t_a \) is the mean-field approximation for the quantum critical point of the transverse Ising model [4].

The leading term of dimerization susceptibility, as follows from the direct numerical (DMRG) calculations of Klümper and co-workers [21], can be reasonably approximated by the bosonization result of Cross and Fisher [21], i.e., \( \eta(x) \approx a_s/x \), where we take \( a_s \approx 0.26 \). Using the above approximation for \( \eta(x) \), we obtain the critical temperature

\[
T_c \approx 4a_s\varepsilon^2/(g_c - g) \tag{7}
\]
as a function of the couplings.

Parameters for Na\( \text{V}_2\text{O}_5 \)—Taking the experimental \( T_c = 34 \text{ K} = 2.93 \text{ meV} \) and a spin-pseudospin coupling of about \( \varepsilon \approx 0.4J_1 = 19.3 \text{ meV} \) we find from Eq. 7 that \( g_c - g \approx 0.132 \text{ eV} \), or \( g/g_c \approx 0.91 \). This estimates for the intrachain Ising coupling implies that Na\( \text{V}_2\text{O}_5 \) is on the disordered side, relatively close to the mean-field quantum critical point of the transverse Ising model. The standard RPA [4, 22] for the transverse Ising model gives the following spectrum of the pseudospin (charge) excitations \( E_q = \sqrt{2t_a[2t_a + m_s g(q)]} \), where the pseudospin average \( m_s = \tanh(t_a/T)/2 \approx \)}
\[ q = 0 \times J \]

FIG. 5: Estimates for the n.n. spin-coupling \( J_1 \) along the ladder, see Eq. (4) from exact diagonalization of the \( 2 \times 4 \) ladder, see Fig. II(a). The parameters are for \( U = 3, t_b = 0.35 \) and various values for \( V_a \) and \( V_b \). For NaV\(_2\)O\(_5\) the hopping \( t_b \) along the leg is about \( t_b \approx 0.175 \).

\[ 1/2 \text{ at } T \ll t_a \text{ and } g(q) \] is the Fourier transform of the Ising coupling. \( E_q \) corresponds to the pole of the retarded pseudospin-pseudospin correlation function \( \langle T^z T^z \rangle(\omega, q) = 2 t_a m_x/ (\omega^2 - E_q^2) \). In the function \( g(q) \) found earlier on the effective 2D lattice \[ 8 \] we retain only the largest intraladder coupling \( g \), so \( (g < g_c) \)

\[ E_{0/\text{quAF}} = 2 t_a \sqrt{1 + g/g_c}. \]

With the above estimates for the couplings we get \( E_0 \approx 0.97 \text{ eV} \approx 7800 \text{ cm}^{-1} \) which agrees well with the observed peak of the optical conductivity \( (q \approx 0) \). At \( q = q_{\text{SAF}} \) corresponding to the SAF ordering wave-vector \( (q_{\text{SAF}} = (0, \pi) \) on the effective 2D square lattice \[ 11 \] we get \( E_{q_{\text{SAF}}} \approx 0.21 \text{ eV} \approx 1700 \text{ cm}^{-1} \).

Discussion—From the Cross-Fisher RPA for the coupled spin-phonon system \[ 21 \], Gros et al have shown \[ 24 \] that a soft mode (i.e., a pole in the phonon-phonon correlation function) occurs at a spin-Peierls transition only if the energy of the involved phonon mode \( \Omega \) is small, namely, \( \Omega < 2.2 T_{\text{SP}} \). The RPA for the coupled spin-pseudospin model renormalizes the pseudospin correlation function as \( D_{zz R}^{-1} = D_{zz}^{-1} - \Pi \) with \( \Pi = -4e^2 q \), resulting in Eq. (6) for the critical temperature of the spin-SAF transition and the same condition for the occurrence of a pole of \( D_{zz R}^{-1} \). A soft antiferroelectric mode is therefore absent in NaV\(_2\)O\(_5\), since \( E_{q_{\text{SAF}}} \approx 210 \text{ meV} > 2.2 T_{\text{e}} = 6.4 \text{ meV} \).

The energy \( 2E_{q_{\text{SAF}}} \approx 3400 \text{ cm}^{-1} \) is quite close to the position of the broad peak near \( 4000 \text{ cm}^{-1} \) observed in the optical absorption experiments at the room temperature \[ 27 \] (see also \[ 2 \] for more detailed data in the frequency range concerned). This suggests that this peak can be attributed to the two-particle (pseudospin) excitations with the ordering wave-vectors.

Conclusions—We have proposed that the spin-SAF transition is of novel kind, in the sense that it is driven directly by the coupling in between spin and orbital degrees of freedoms. We have presented support for this scenario from numerical estimates for the coupling parameters and proposed an mechanism for a hitherto unexplained feature in the infrared spectrum. These studies might be of relevance for other materials with strong spin-orbital couplings.

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