Test of the frustrated spin-cluster model to describe the low-temperature physics of NaV_2O_5

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Recent experimental evidence suggests the existence of three distinct V-valence states (V^{4+}, $V^{4.5+}$, and V^{5+}) in the low-temperature phase of NaV_2O_5 in apparent discrepancy with the observed spin gap. We investigate a spin cluster model, consisting of weakly coupled, frustrated four-spin clusters aligned along the crystallographic *b* axis that was recently proposed to reconcile these experimental observations. We have studied the phase diagram and the magnon dispersion relation of this model using DMRG, exact diagonalization, and a cluster-operator theory. We find a spin gap for all parameter values and two distinct phases, a cluster phase and a Haldane phase. We evaluate the size of the gap and the magnon dispersion and find no parameter regime which would reproduce the experimental results. We conclude that this model is inappropriate for the low-temperature regime of NaV_2O_5.

Introduction. Recent investigations of electronically quasi-one-dimensional (1D) transition metal compounds probe the limits of our understanding of the interplay between structural and electronic effects in such low-dimensional materials. In NaV_2O_5, a prototypical example for this class of materials, V ions are arranged in ladders along the crystallographic *b* direction. Measurements of the magnetic susceptibility[1] in the high-temperature phase indicate the presence of only one equivalent V site[2,3] with valence $V^{4.5+}$, consistent with a model where the electrons in bonding V-O-V orbitals along the rungs of the ladder form a 1D Heisenberg chain.[2,4]

At $T_C = 34$ K the unit cell doubles along the *a* and *b* and quadruples along the *c* axis[5] in a phase transition of as-of-yet unknown origin. At the same time a spin-gap of $\Delta_{min} = 10$ meV opens[1] and charge ordering $2V^{4.5+} \rightarrow V^{4+} + V^{5+}$ sets in.[6] The observed charge ordering is inconsistent with a generic spin-Peierls scenario[1] and raises the question about the driving force (lattice, magnetic, or Coulomb) responsible for this transition. Since NaV_2O_5 is an insulator, the discussion of the material is simplified by the introduction of pseudospins for the charge degrees of freedom that couple to the spin degrees of freedom.[7–10] The effective spin Hamiltonian depends, consequently, on the pattern of charge order[11] and may differ in the high- and the low-temperature phase.

The occurrence of two well defined magnon-branches for $T < T_C$ in NaV_2O_5 along the *a* direction (perpendicular to the chains), as measured by neutron scattering,[12] had been explained tentatively by a model, where the charge orders in a ''zig-zag'' pattern in the low-temperature phase.[11] This proposal has been questioned by recent analysis of the low-temperature crystal structure.[13,14] Based on bond-charge models, the existence of three different V-valence states (V^{4+}, $V^{4.5+}$, and V^{5+}) has been proposed,[15,14] as illustrated in Fig. 1. In this analysis, pairs of $V^{4.5+}$ form dimerized spin chains on every other ladder, which alone could explain the observed spin gap.[11] A puzzle is posed however, by the presence of free isolated moments on the V^{4+} ions on the remaining ladders, which is inconsistent with the existence of such a gap.

As one possible reconciliation, Boer *et al.*[14] recently proposed that the V^{4+} moments are quenched by their interaction with the neighboring $V^{4.5+}$ sites of the adjacent dimerized V-O-V ladder. Within this model, clusters of six vanadiums each (and with four spins) would be weakly coupled and the observed spin-gap would arise not from the dimerization but locally from the gap of the isolated clusters.

To distinguish between these fundamentally different mechanisms we study this model by a series of complementary approaches, using DMRG,[16] exact diagonalization and a bond-cluster theory, to map all physically relevant regions of

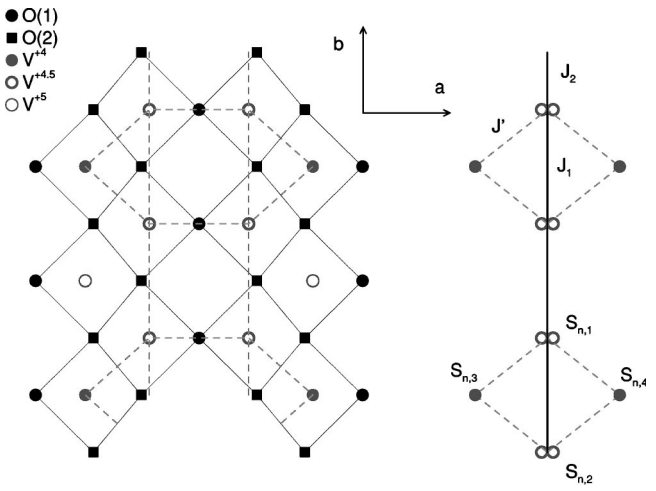

FIG. 1. The spin-cluster model for NaV_2O_5. On the left the charge valency in one V-O plane (Refs. 15 and 14). The dashed lines indicate the proposed dominant interactions. Note that $V^{4+} \hat{=} (3d)^1$, $V^{4.5+} \hat{=} (3d)^{0.5}$, and $V^{5+} \hat{=} (3d)^0$. On the right is the proposed cluster spin model (Ref. 14). Note, that two $V^{4.5+}$ on one rung share one electron.

its phase diagram. We find that the ground-state varies continuously from a cluster phase for large J' to a Haldane phase for small J' (see Fig. 1). We evaluate the gap and the dispersion and find that there is no parameter regime that would explain the neutron-scattering data.[12]

The spin-cluster model. We denote by $\mathbf{S}_{n,i}$ $(i=1,\ldots,4)$ the four spins of the nth cluster, compare Fig. 1. The Hamiltonian is then

$$H=J_1\sum_n \mathbf{S}_{n,1}\cdot\mathbf{S}_{n,2}+J_2\sum_n \mathbf{S}_{n,1}\cdot\mathbf{S}_{n+1,2}$$

$$+J'\sum_n (\mathbf{S}_{n,1}+\mathbf{S}_{n,2})\cdot(\mathbf{S}_{n,3}+\mathbf{S}_{n,4}), \qquad (1)$$

where $J_1=J(1+\delta)$ and $J_2=J(1-\delta)$ (with $J_1,J_2,J'>0$). δ is the degree of dimerization. For $J'=0$ the $\mathbf{S}_{n,1/2}$ form a dimerized chain with an in-chain gap $\sim J\delta^{2/3}$. A particular property of Eq. (1) is the local coupling to the total spin $\mathbf{S}_{n,3}+\mathbf{S}_{n,4}$, which is consequently a (locally) conserved quantity, $(\mathbf{S}_{n,3}+\mathbf{S}_{n,4})^2=S_n(S_n+1)$ for any n. In the ground state $S_n\equiv 1$. A related model with $J_1=0$ and a coupling between $\mathbf{S}_{n,3}$ and $\mathbf{S}_{n,4}$ has been studied by Richter *et al.*[17]

We consider first an isolated cluster and denote by s_{ij} and t^α_{ij} the wave functions of the singlet and of the triplets ($\alpha=-1,0,+1$) of the spins i and j $(i,j=1,\ldots,4)$. The low-energy states are

$$\psi_1=\frac{1}{\sqrt{3}}[t^0_{12}t^0_{34}-t^+_{12}t^-_{34}-t^-_{12}t^+_{34}], \qquad (2)$$

$$\psi_2=s_{12}s_{34}, \quad \psi^\alpha_3=s_{12}t^\alpha_{34}, \qquad (3)$$

$$\psi^0_4=\frac{1}{\sqrt{2}}[t^+_{12}t^-_{34}-t^-_{12}t^+_{34}], \qquad (4)$$

where ψ^0_4 is the $S^z=0$ component of the triplet ψ^α_4. The corresponding energies are $E_1=-2J'+J_1/4$, $E_2=E_3=-3J_1/4$, and $E_4=-J'+J_1/4$.[18]

For $J'/J_1>0.5$ the singlet ψ_1 is the ground state (we denote this region the ''cluster phase''). For $J'/J_1<0.5$ the ground state of the isolated cluster is fourfold degenerate, the singlet ψ_2 and the triplet ψ_3 have the same energy. Note that the intercluster coupling J_2 will not mix ψ_2 and ψ_3, since the local spin $\mathbf{S}_{n,3}+\mathbf{S}_{n,4}$ is conserved. Intercluster coupling J_2 will lead to an antiferromagnetic interaction $J_H\sim(J'J_2)^2/J_1^3$ between the moments of the ψ_3 states, as can be evaluated easily in second-order perturbation in J_2 (using the complete set of eigenstates of the cluster). The total energy is therefore lowered by J_2 when all cluster states are ψ_3. The $S=1$ moments of the ψ_3 states thus form an effective spin-1 chain with a Haldane gap $\Delta_H=0.410\,50J_H$.[19] We denote this region therefore the ''Haldane phase.''

We have evaluated the energy gap of the spin-cluster model by DMRG,[16] using the finite-size algorithm with open boundary conditions for systems with $L=32$ and $L=64$ spins. The ground state has $N_\uparrow=L/2$ up spins and $N_\downarrow=L/2$ down spins. We retained typically 60 states of the density matrix, checking the convergence by additional calculations with 40 and 90 states, respectively. We evaluated the gap by

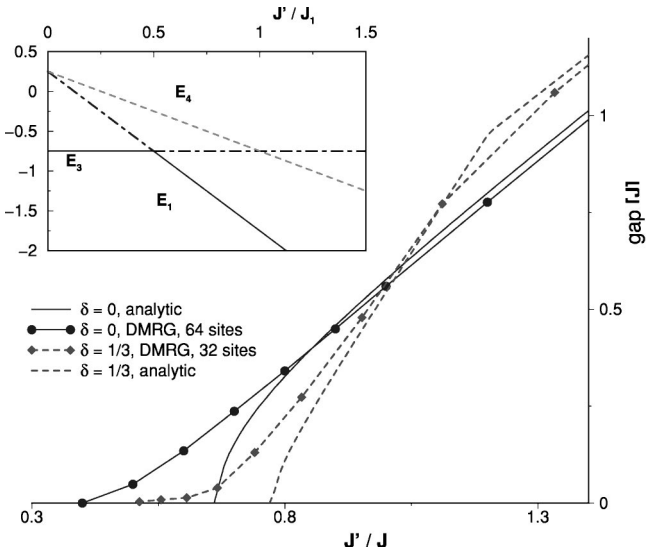

FIG. 2. The (singlet-triplet) gap in units of J for fixed $\delta=0$ and $\delta=1/3$ as a function of J'. Filled Symbols: DMRG data. Lines: Results from the cluster operator theory. Inset: The three low-lying energy levels E_1, E_3, and E_4 for an isolated cluster in units of J_1 as a function of J'/J_1. The corresponding wave functions ψ^α_3 and ψ^α_4 are triplets, ψ_1 is a singlet.

two complementary methods, namely (i) by targeting two states in the sector with $N_\uparrow=L/2=N_\downarrow$ and (ii) by targeting the ground states in (a) the sector with $N_\uparrow=L/2=N_\downarrow$ and (b) $N_\uparrow=L/2+1$ and $N_\downarrow=L/2-1$. We find complete consistency and present the results in Fig. 2 for some selected values for the dimerization δ. The finite-size corrections are smaller than the symbol sizes. We find a rapidly decreasing gap as a function of decreasing J'/J and a smooth crossover between the cluster and the Haldane phase. As the symmetry of these two phases is the same, we do not expect a phase transition in the thermodynamic limit.

Cluster-operator theory. In the cluster phase two low-lying triplet modes, ψ^α_3 and ψ^α_4, are relevant. In order to take the effect of the intercluster coupling J_2 into account we describe the seven degrees of freedom of cluster n by bosonic degrees of freedom: $s^\dagger_n$ for the singlet (ψ_1) $b^\dagger_{n,3,\alpha}$ and $b^\dagger_{n,4,\alpha}$ for the triplets (ψ_3 and ψ_4). The low-lying singlet ψ_2 does not couple and may be disregarded here. This approach generalizes the bond-operator theory for dimerized spin chains[20] to the case of spin clusters. The constraint $s^\dagger_n s_n+\Sigma_{\tau,\alpha}b^\dagger_{n,\tau,\alpha}b_{n,\tau,\alpha}=1$ $(\tau=3,4)$ restricts the bosonic Hilbert space to the physical one. The spin operators take the form

$$S^z_{n,1/2}=\pm\frac{b^\dagger_{n,3,0}s_n+s^\dagger_n b_{n,3,0}}{\sqrt{12}}-\frac{b^\dagger_{n,4,0}s_n+s^\dagger_n b_{n,4,0}}{\sqrt{6}}. \qquad (5)$$

Note, that there are no terms $\sim b^\dagger_{n,\tau,\alpha}b_{n,\tau',\alpha'}$ corresponding to triplet-triplet interactions. In linearized Holstein-Primakov approximation (LHP), we substitute $s^\dagger_n\to 1$ and $s_n\to 1$ in Eq. (5) and in similar expressions for $S^{x/y}_{n,1/2}$. This approximation retains spin-rotational invariance and we may disregard the index $\alpha=-1,0,1$ for the triplet operators. We obtain for the LHP Hamilton operator in momentum space $H^{(LHP)}=H_0+H^{(1)}_2+H^{(2)}_2$ with $H_0=\Sigma_{k,\tau}\Delta_\tau b^\dagger_{k,\tau}b_{k,\tau}$ $(\Delta_\tau=E_\tau-E_1)$. The intercluster coupling is given by

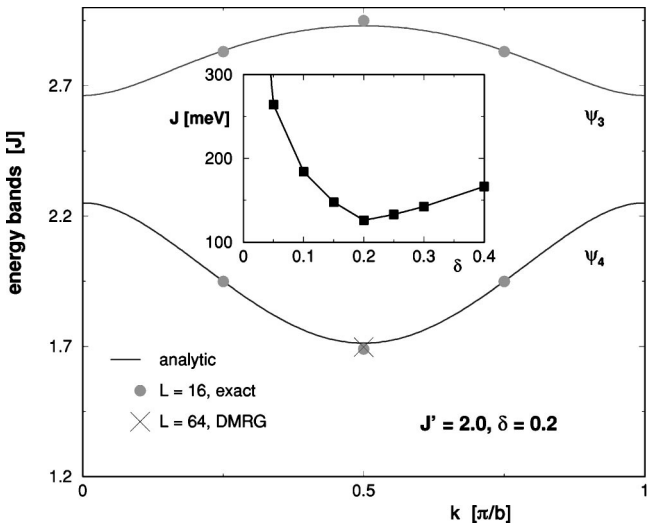

FIG. 3. The magnon dispersion for $J'=2J, \delta=0.2$. Note the zero of energy. The lines are the result of the cluster-operator theory, the circles of an exact diagonalization study with 16 spins (periodic boundary conditions). The cross denotes the DMRG result. Inset: The value of J as a function of dimerization δ needed to fit the measured dispersion of NaV_2O_5 (LHP result, for $J/2<J'<J$).

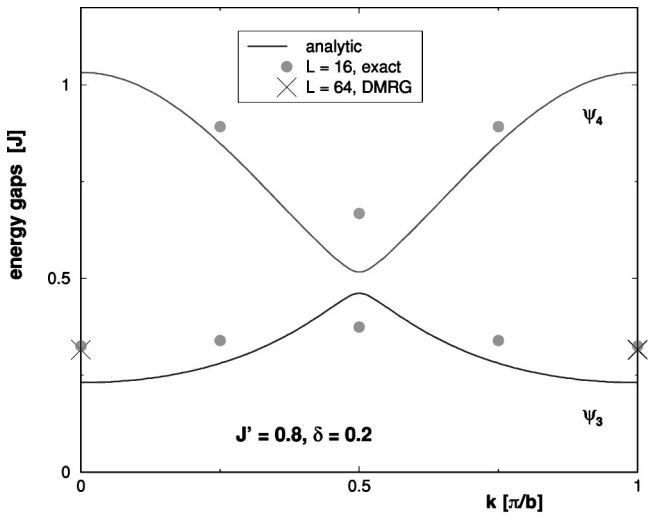

FIG. 4. The magnon dispersion for $J'=0.8J, \delta=0.2$. The symbols are as in Fig. 3. Note that the cluster-operator theory overestimates the magnon dispersion.

$$H_2^{(1)}=\frac{J_2}{12}\sum_k\,[2\cos(2bk)(2b^\dagger_{k,4}b_{k,4}-b^\dagger_{k,3}b_{k,3}) + i2\sqrt{2}\sin(2bk)(b^\dagger_{k,3}b_{k,4}-b^\dagger_{k,4}b_{k,3})] \tag{6}$$

and

$$H_2^{(2)}=\frac{J_2}{12}\sum_k\,[\cos(2bk)(2b^\dagger_{-k,4}b^\dagger_{k,4}-b^\dagger_{-k,3}b^\dagger_{k,3}) - i2\sqrt{2}\sin(2bk)b^\dagger_{k,4}b^\dagger_{-k,3}+\text{H.c.}]. \tag{7}$$

Here $b=3.611$ Å is the lattice constant of the high-temperature phase. Note the opposite sign in the dispersion of two triplets. It is straightforward to diagonalize $H^{(LHP)}$. We define $c=(J_2/6)\cos(2bk)$, $2t=\Delta_4^2+\Delta_3^2+2c(2\Delta_4-\Delta_3)$, and $s=\Delta_3^2\Delta_4^2+2c\Delta_3\Delta_4(2\Delta_3-\Delta_4)-2\Delta_3\Delta_4J_2^2/9$. The dispersion $\omega_\pm=\omega_\pm(k)$ of the two magnon branches (each branch is threefold degenerate) in LHP approximation is then

$$\omega_\pm^2=t\pm\sqrt{t^2-s}. \tag{8}$$

We have included the results for the magnon gap in Fig. 2. For large ratios J'/J the LHP result becomes asymptotically exact, in this limit it is equivalent to perturbation theory in J_2. In the LHP approximation the transition to the Haldane phase is signaled by a vanishing of the energy gap, the crossover cannot be described by the cluster-operator theory.

In Fig. 3 we present the magnon-dispersion Eq. (8) for $J'=2J$ and compare the LHP results (lines) with an exact-diagonalization study of a system with 16 sites (filled circles).[21] The agreement is very good, due to the large gap and (correspondingly) small correlation length. Note that the low-lying magnon, which corresponds to ψ_4 (see inset of Fig. 2), has its minimum at $k=\pi/(2b)$.

In Fig. 4 we present the magnon-dispersion Eq. (8) for $J'=0.8J$ which is closer to the transition to the Haldane phase. The agreement with the exact diagonalization and the DMRG data is not good, since the precursors to the Haldane phase are not included in the cluster-operator theory. The low-lying magnon, which corresponds to ψ_3 (see inset of Fig. 2), has its minimum now at $k=0$ and $k=\pi/b$ and a maximum at $k=\pi/(2b)$, as measured by neutron scattering.[12] The cluster-operator theory substantially overestimates the size of the magnon dispersion relative to the exact-diagonalization result near to the Haldane phase. The physical reason for this discrepancy can be understood: The lattice constant of the effective spin-1 chain in the Haldane phase is $2b$ and the minimum of the magnon dispersion is therefore at $\pi/(2b)$ in the Haldane phase.[22] It changes therefore at the crossover from the cluster phase and the Haldane phase. This change in the location of the gap is not included in the cluster-operator theory.

Discussion. The exchange constant along b is $J\approx 529-560$ K (Refs. 1 and 23) in the high-temperature phase of NaV_2O_5 and the interladder coupling is probably very small, a $J'/J\approx 1/45$ has been found in an analysis of the magnon dispersion for $T<T_C$ in a model with zig-zag charge order.[11] This small ratio is consistent with the very small coupling along a found in a LDA study.[2] There are, however, two reasons why J' might be larger in the low-temperature phase. (a) As noted by Horsch and Mack,[4] there is a near cancellation for $T>T_C$ in between paths with intermediate singlet and triplet states and energies $E_{s/t}$: $J'=0.5t_{xy}^2(1/E_s-1/E_t)$, where t_{xy} is the V-V hopping matrix element in a direction. A corresponding calculation for $T<T_C$ in the phase shown in Fig. 1 yields $J'=t_{xy}^2(1/E_s+1/U-1/E_t)$ (U is the onsite Hubbard U). (b) t_{xy} might be substantially larger in the low-temperature phase, since the smallness of t_{xy} for $T>T_C$ is a subtle band-structure effect.[2] We have therefore scanned the complete phase diagram of the spin-cluster Hamiltonian in order to determine whether there exists a parameter range able to fit the neutron-scattering data.

We have tried to reproduce, within the spin-cluster model, four known properties of NaV_2O_5: (i) The gap (averaged over k_a) is $\Delta_{min}=10$ meV. (ii) The maximum of the disper-

sion of the lowest magnon branch is at $\pi/(2b)$, the minimum at 0 and π/b. (iii) The value of the maximum of the dispersion of the lowest magnon branch is $\Delta_{max} \approx 40$ meV,[12,24] i.e., the ratio is $\Delta_{max}/\Delta_{min} \approx 4$. (iv) The value of the coupling along b is $J \approx 441$ K$=38$ meV for $T < T_{SP}$.[12,25]

Condition (ii) implies that only the cluster phase of Hamiltonian Eq. (1) with $J' < J_1$ is a candidate for the low-temperature phase of NaV_2O_5. This implies $J_1/2 < J' < J_1$. Within the cluster-operator theory one obtains $\Delta_{max}/\Delta_{min} = 4$ for values of J' near to the gap closing. One needs consequently large coupling constants J (see inset of Fig. 3) in order to reproduce $\Delta_{min} = 10$ meV. We have evaluated the values of J' and J needed to reproduce the gap ratio as a function of dimerization δ and find a minimum in J for $\delta = 0.2$ (see inset of Fig. 3). This minimum is $J \approx 126$ meV, substantially larger than the experimental value $J \approx 38$ meV. Note, that the cluster-operator theory overestimates the dispersion in this phase and *underestimates* the value of J needed. We therefore conclude safely, that the model is not able to reproduce the measured magnon dispersion of NaV_2O_5 and that Eq. (1) is unlikely to be the appropriate model for the low-temperature phase of NaV_2O_5, at least in its one-dimensional version. It might be possible, in principle, that two-dimensional couplings change the scenario obtained in the present study, though we note, that an increase in dimensionality does, in general, reduce the size of a spin gap.

Note added in proof. The same model as in Eq. (1) has been considered in Refs. 26 and 27.

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