PHYSICAL REVIEW B VOLUME 62, NUMBER 22 1 DECEMBER 2000-II

Spin-cluster model for the low-temperature phase of α'-NaV_2O_5

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(Received 21 August 2000)

We discuss magnetic excitations of a spin-cluster model which has been suggested to describe the low-temperature phase of α'-NaV_2O_5. This model fulfills all symmetry criteria proposed by recent x-ray investigations. We find that this model is not able to describe the occurrence of two well separated magnon lines perpendicular to the ladder direction as observed in inelastic neutron scattering experiments. We suggest further experimental analysis to generally distinguish between models with double reflection or inversion symmetry.

The modeling of the low-temperature phase of NaV_2O_5 has initiated a discussion of effective spin models for the low-lying magnetic excitations. NaV_2O_5 undergoes a phase transition at $T_c = 34$ K,[1] associated with a lattice distortion, charge ordering, and the opening of a spin gap. In NaV_2O_5 the V ions are arranged in staggered ladders along the crystallographic b axis. While in the high-temperature phase there is only one $V^{4.5+}$ site, recent x-ray diffraction studies[2–4] suggest that in the low-temperature phase there are three distinct valence states: on every other ladder one finds a zig-zag charge ordering of V^{4+} and V^{5+} valence states, while on the intermediate ladders one finds rungs with two $V^{4.5+}$ sites. The structural investigation further indicates that the space group of the low-temperature phase is $Fmm2$. In the a-b plane one finds a doubling of the unit cell along **a** and **b** as well as mirror planes $\perp$ **a** and $\perp$ **b**. The latter criterion generally excludes models with dimerization along in-line[5] or zig-zag chains.[6,7]

Recent inelastic neutron scattering experiments[9] show that there are two close-by magnon excitations with a gap of 8.75 meV and 10.65 meV. Both excitations have a large dispersion along the b axis. The magnetic exchange coupling along **b** has been estimated to range between 37.9 meV and 60 meV.[8,9] The dispersion along **a** shows only a weak modulation of about 0.5 meV which is out of phase for the two well separated branches. Raman scattering experiments[10] observe three excitations below the two magnon continuum which have been interpreted as singlet excitations. Remarkably, the lowest excitation has a gap that seems to coincide with the gap of the lower branch of the two magnon excitations.

Based on recent x-ray diffraction experiments in the low-temperature phase, de Boer *et al.*[3] proposed the formation of weakly coupled, frustrated spin-clusters along the crystallographic b axis.[11] Each cluster (see Fig. 1) contains six vanadium atoms distributed over three ladders and an overall number of four unpaired electrons which form a singlet ground state. The spin-cluster model is one of the proposed models that obey double reflection symmetry.

A previous theoretical study[12] addressed the applicability of the one-dimensional arrangement to model the strong magnon dispersion along the crystallographic b axis. Using a novel cluster-operator theory as well as exact diagonalization and density-matrix renormalization group calculations, the authors concluded that there is no parameter regime which would reproduce the observed b-axis dispersion.

In this paper, we present a study of the proposed spin-cluster model by means of a strong-coupling expansion. We calculate high order results for the magnon dispersions along the b axis as well as the leading contribution along the a axis. We discuss several mechanisms to explain the occurrence of two low lying magnon branches without finding a profound supporting argument. We point out that symmetries of the magnon dispersions can be used to distinguish between classes of models with reflection and inversion symmetry. Further, we study the occurrence of singlet states in the spin-cluster model in terms of the reported Raman observations. We find that there is no evidence for a low lying singlet excitation of comparable energy to the lowest triplet excitation.

The Hamiltonian of the spin-cluster model reads

$$\begin{aligned} H = {} & J_1 \sum_n \mathbf{S}_{1,n}\cdot\mathbf{S}_{2,n} + J_2 \sum_n \mathbf{S}_{1,n}\cdot\mathbf{S}_{2,n+1} \\ & + J' \sum_n (\mathbf{S}_{1,n}+\mathbf{S}_{2,n})\cdot(\mathbf{S}_{3,n}+\mathbf{S}_{4,n}) \\ & + J_3 \sum_n (\mathbf{S}_{2,n}\cdot\mathbf{S}'_{3,n} + \mathbf{S}_{4,n}\cdot\mathbf{S}'_{1,n} + \mathbf{S}_{4,n}\cdot\mathbf{S}'_{2,n+1} \\ & + \mathbf{S}_{1,n}\cdot\mathbf{S}'_{3,n+1}), \end{aligned} \tag{1}$$

where the $\mathbf{S}_{i,n}$ and $\mathbf{S}'_{i,n}$ denote the four spins on the nth cluster of two neighboring b axis chains. $J_1 = (1+\delta)J$ and $J_2 = (1-\delta)J$ are alternating interactions along the b axis and J_3 is the interaction along the a-axis. All interactions J, J', and J_3 are assumed to be antiferromagnetic.

For an isolated cluster, $J_2 = J_3 = 0$, we have two singlet, three triplet, and one quintuplet eigenstates. We denote the low-lying eigenstates as follows:

$$\begin{aligned} \psi_1 &= \frac{1}{\sqrt{3}}[t_{12}^{+}t_{34}^{-} + t_{12}^{-}t_{34}^{+} - t_{12}^{0}t_{34}^{0}], \\ \psi_2 &= s_{12}s_{34}, \quad \psi_3^{\alpha} = s_{12}t_{34}^{\alpha}, \\ \psi_4^{0} &= \frac{1}{\sqrt{2}}[t_{12}^{-}t_{34}^{+} - t_{12}^{+}t_{34}^{-}], \end{aligned} \tag{2}$$

where s_{ij} and t_{ij}^{α} are singlet and triplet states of the spins at sites i and j, and ψ_4^0 is the $S^z = 0$ component of the triplet

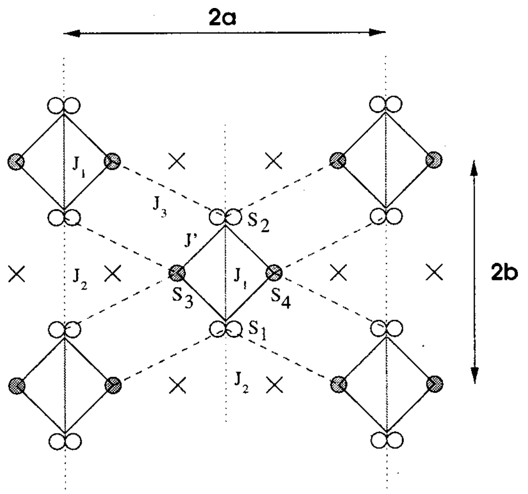

FIG. 1. The spin-cluster model. The filled circles denote V^{4+} ions, the crosses denote V^{5+} ions and the open circles denote pairs of $V^{4,5+}$ ions.

ψ_4^α. The corresponding energies are $E_1=-2J'+\frac{1}{4}J_1$, $E_2=E_3=-\frac{3}{4}J_1$ and $E_4=-J'+\frac{1}{4}J_1$.

The ground state of the spin cluster is the singlet state ψ_1 for antiferromagnetic couplings J and J' with $J'>\frac{1}{2}J_1$. For smaller values of J', the ground state lies in the fourfold degenerate manifold of the states ψ_2 and ψ_3^α. In first order, the intercluster coupling J_2 lowers the energy of the ψ_3 states while leaving the ψ_2 states unchanged. One thereby obtains an effective $S=1$ Heisenberg chain with a Haldane gap at $\pi/(2b)$.

In the following we will focus on the first parameter regime where ψ_1 is the only ground state. For an isolated cluster there are two low energy triplet excitations ψ_3 and ψ_4. To calculate their dispersion along **b** we perform a strong-coupling expansion[13,14] around the isolated cluster limit treating

$$H_1=J_2\sum_n \mathbf{S}_{1,n}\cdot\mathbf{S}_{2,n+1} \tag{3}$$

as a perturbation. For the moment we neglect the interchain coupling J_3 which we assume to be significantly smaller than J due to the longer exchange path along **a**. We have calculated series up to order 7 in J_2/J_1 where the largest system taken into account contains $L=32$ spins.

The two triplet dispersions are well separated for large values of J' as shown in Fig. 2. Here the obtained series are very well converged already in second order. Our results are consistent with those of the reported exact diagonalization and DMRG calculations, whereas the results of the linearized Holstein-Primakov approximation (LHP) used in the cluster-operator theory[12] disagree slightly for momenta in the region around $k=0$.

The perturbative Hamiltonian H_1 strongly intermixes the two magnon excitations ψ_3 and ψ_4. For small values of the cluster exchange J' and the dimerization δ we find that the two energy bands are very close by for intermediate momenta $0<k_y<\pi/(2b)$ as shown in Fig. 3.

We have calculated effective Hamiltonians for the two excitations separately as well as a combined effective Hamiltonian treating the excitations on the same footing. We thereby consider the repulsive interaction between the two energy bands. While the first approach suffers a breakdown of the perturbation expansion due to small energy denominators in momentum regions where the two mixing magnon excitations are nearly degenerate, it allows the assignation of the nature of the excitation at $k_y=\pi/(2b)$. For example, we find that for $J'=1.1$, J_1 and $\delta=0.5$, the lower energy at $k_y=0$ corresponds to a ψ_3 excitation, whereas at $k_y=\pi/(2b)$ the lower excitation corresponds to a ψ_4 excitation. In Fig. 3 we have used D log Padé approximants[15] which extrapolate the calculated finite series to flatten out the occurring singularities (dashed lines).

The second approach allows the explicit calculation of the mixing between the two excitation branches. We find that there is strong band repulsion for the whole parameter range.

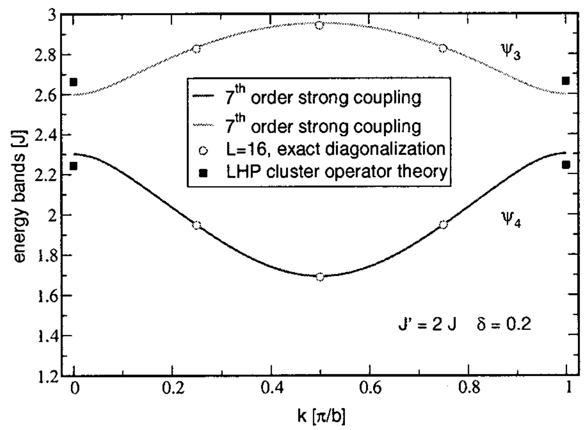

FIG. 2. The magnon dispersion for $J'=2J$, $\delta=0.2$. The solid lines are the result of the seventh order strong coupling expansion, the open circles are exact diagonalization results, and the squares denote the results from the cluster operator theory from Ref. 12.

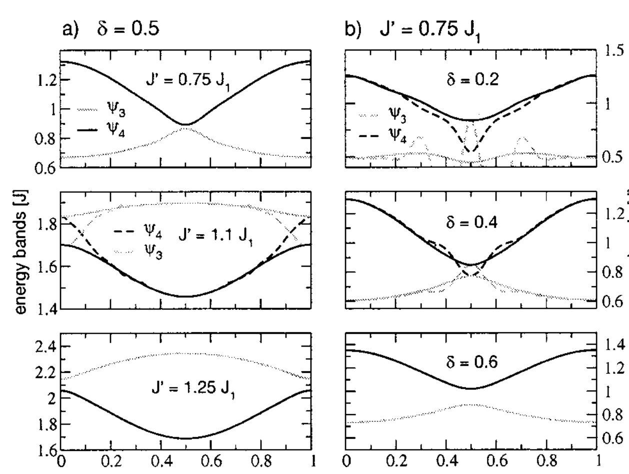

FIG. 3. The ψ_3 and ψ_4 magnon dispersions. In the left column the cluster interaction J' is varied for a constant dimerization δ. In the right column δ is varied keeping J' constant. A strong mixing of the two branches is observed. Dlog Padé approximants (dashed lines) have been used to extrapolate the series obtained treating the excitations separately. The solid lines are results of a combined calculation considering the band repulsion. For $\delta=0.2$ we find only a very limited convergence.

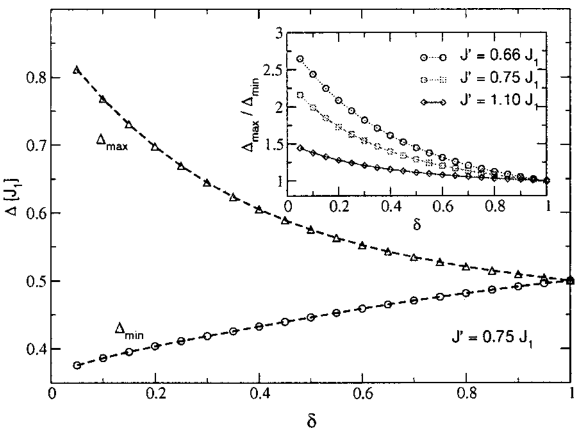

FIG. 4. The maximum Δ_{max} of the ψ_3-excitation at $k_y = \pi/(2b)$ and the gap Δ_{min} at $k_y=0$ for $J'=0.75\ J_1$ versus dimerization δ. The inset shows the ratio $\Delta_{max}/\Delta_{min}$ for varying values of J' and δ.

For those parameter sets where in the first approach the extrapolated dispersions cross we now find two well separated branches, but the nature of the excitation changes depending on the momentum.

Neutron scattering experiments observe the spin gap at the antiferromagnetic point $k_y^{AF}=\pi/b$ and the zone center $k_y^{ZC}=0$, which would correspond to a ψ_3 excitation in the spin-cluster model. This assignment enables us to determine the ratio of Δ_{max} at $k=\pi/(2b)$ to the gap Δ_{min} at $k=0$, in order to clarify whether an observed gap value of around 10 meV is consistent with an estimate of 40 to 60 meV for the spin exchange J. In Fig. 4 we show the calculated values at the respective momenta for $J'=0.75\ J_1$ as a function of dimerization δ. For small values of δ the results of the strong coupling expansion are less reliable, but it seems that a ratio of 4 does not disagree with our results. A tentatively estimated parameter set of $J'=0.66\ J_1$ and $\delta=0.05$, would give a ratio of around 3 and a spin gap of around 0.25 J_1 which was doubted in a previous theoretical analysis.[12]

Nevertheless, we point out that the shape of the ψ_3 dispersion is rather flat in the vicinity of $k_y=0$ and $k_y=\pi/b$, which is due to the strong band repulsion. This seems to contradict the experimental observations of a steep ascent.[8,9] Further, we note that for these parameters the minimum of the ψ_4 excitation at $k_y=\pi/(2b)$ is of comparable size to the actual spin gap, but has not been reported by neutron scattering experiments.

The leading contribution to the dispersion of the low-lying ψ_3-magnon excitation along **a** is given by the spin exchange mediated by an interaction J_3 between neighboring spin clusters (see Fig. 1):

$$\epsilon_{ab}(\mathbf{k}_x,\mathbf{k}_y)=\epsilon_b(\mathbf{k}_y)+\frac{J' J_3^2}{3J_1(J_1-2J')}\cos(\mathbf{k}_x\cdot\mathbf{a})\cos(\mathbf{k}_y\cdot\mathbf{b}). \tag{4}$$

The spin-cluster model inherently produces a leading periodicity of $2\pi/a$ for the dispersion along **a**. This corresponds to the periodicity observed in inelastic neutron scattering (INS) experiments[8,9] and is consistent with a primitive unit cell of area $2ab$ as reported by structural x-ray investigations[3] taking into account the π/b periodicity along **b**. The ψ_3 magnon on an isolated cluster consists of a singlet state s_{12} along the b-axis bond. We therefore expect a strong coupling to scattering neutrons at the antiferromagnetic point $k_y^{AF}=\pi/b$ and only a strongly suppressed signal in the vicinity of the zone center at $k_y^{ZC}=0$. According to Eq. (4) the modulation of the magnon dispersion along **a** is out of phase for these choices of k_y.

Recent neutron scattering experiments[9] report the observation of two close by, but well separated, out of phase magnon branches. The spin-cluster model at hand gives only one low lying magnon branch with the observed periodicity. This excludes a simple spin-Peierls scenario to explain the occurrence of *two* out of phase magnon branches, e.g., folding back a single magnon branch with double periodicity as it was suggested for a zig-zag model in Ref. 16.

A way of explaining the occurrence of two close by magnon branches in this model is to consider an anisotropic exchange interaction. An *xxz* anisotropy could lift the triplet degeneracy in a single branch and a doublet branch. Experimentally, this splitting of a single triplet branch should result in a 1:2 ratio of neutron scattering intensities which has not been reported.[9] Further, a magnetic field would cause the doublet line to split which has not been confirmed by optical spectroscopy.[10]

The investigation of the spin-cluster model reveals some aspects that should be covered by future neutron scattering experiments, namely the experimental evidence of asymmetric couplings and a verification of the basic symmetries found in x-ray scattering.

Besides a careful investigation of the scattering intensities of the two magnon branches, polarized neutron scattering experiments could give evidence for the splitting of a single magnon line, thereby proving the existence of anisotropic couplings.

The verification of the basic symmetries by means of neutron scattering experiments is experimentally far less sophisticated. The spin-cluster model is symmetric under reflections along the mirror planes $\perp\mathbf{a}$ and $\perp\mathbf{b}$. Accordingly, the obtained dispersion $\epsilon_{ab}(k_x,k_y)$ is symmetric under transformations of $k_x\to -k_x$ and $k_y\to -k_y$. The experimental data of the dispersion along **a** for $k_y=0$ and $k_y=\pi/b$ seem to be symmetric under the reflection $k_x\to -k_x$. Nevertheless, we point out that scanning along an arbitrary value of k_y will allow us to distinguish between models obeying double reflection symmetry and inversion symmetry. For the latter we generally expect an unsymmetric dispersion for intermediate k_y, whereas for models with double reflection symmetry we expect a cosine modulation of the amplitude of a symmetric dispersion along **a** as given in Eq. (4).

For a single spin cluster, there is one low-lying singlet excitation ψ_2 which is degenerate with the triplet excitation ψ_3. For vanishing interchain coupling J_3 the Hamiltonian (1) is symmetric under a *local* interchange of $\mathbf{S}_{3,n}$ and $\mathbf{S}_{4,n}$. The perturbation operator H_1 also conserves this local symmetry. A direct product state of ψ_1 states which are even under this symmetry and a ψ_2 excitation at some arbitrary cluster which is odd under this symmetry couples to a variety of states with the same local symmetries, but does not allow the singlet excitation ψ_2 to move. Though the energy of this excitation will be changed, it will not gain any dispersion. As a consequence the original degeneracy with the triplet excitation ψ_3 is lifted. Neglecting the interaction along the *a* axis we have calculated the energy of the singlet ψ_2 up to order 10 in J_2/J_1. It turns out that the ratio of the obtained energy to the gap of the elementary triplet excitation is very consistent with the expected value of 1.6 for the *higher* singlet excitation at 107 cm^{-1} as measured in Raman spectroscopy.

To explain the occurrence of a low lying Raman excitation at 66 cm^{-1} (8.3 meV),[10] we have estimated the binding energies of two-magnon singlet bound states built of the elementary triplet excitations ψ_3 and ψ_4. We find that in leading order there is no substantial renormalization of these energies and we conclude that these bound states are close to the two-magnon continuum at ~ 132 cm^{-1} and are not sufficient to explain the occurrence of the low lying Raman excitation. Recent electron spin resonance (ESR) studies show evidence for a Dzyaloshinskii-Moriya interaction below 20 K.[17,18] The inclusion of spin-orbit coupling might explain the observation of a Raman excitation degenerate to the spin gap.

In conclusion, we have calculated the magnetic excitations of a spin-cluster model. We find only partial agreement with the experimentally observed spectrum. Along the crystallographic *b* axis there are two strongly intermixing magnon bands in the parameter regime relevant for NaV_2O_5. Due to strong band repulsion we find that the lower magnon branch exhibits a weaker dispersion than experimentally observed. Further, the purely magnetic model leads to only one magnon branch with the observed periodicity along the *a* axis. We find one low lying singlet state which matches the energy of one of the observed Raman excitations. While the prevailing models for the low temperature phase of NaV_2O_5 are inversion symmetric, the spin-cluster model obeys double reflection symmetry. To generally distinguish between these models we propose further experiments scanning the magnon dispersions along **a** for arbitrary values of k_y.

We thank Girsh Blumberg for many valuable discussions. S.T. was supported in part by the German National Merit Foundation.

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