

A new view of the electronic structure of the spin-Peierls compound α' - NaV_2O_5 *

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Abstract. The present understanding of the electronic and magnetic properties of α' - NaV_2O_5 is based on the hypothesis of strong charge disproportionation into V^{4+} and V^{5+} , which is assumed to lead to a spin-1/2 Heisenberg chain system. A recent structure analysis shows, however, that the V-ions are in a mixed valence state and indistinguishable. We propose an explanation for the insulating state, which is not based on charge modulation, and show that strong correlations together with the Heitler-London character of the relevant intermediate states naturally lead to antiferromagnetic Heisenberg chains. The interchain coupling is weak and frustrated, and its effect on the uniform susceptibility is found to be small.

PACS. 75.50.Ee Antiferromagnetics – 75.30.Et Exchange and superexchange interactions – 75.40.Cx Static properties (order parameter, static susceptibility, heat capacities, critical exponents, etc.)

One-dimensional spin-1/2 Heisenberg antiferromagnets are expected to undergo a structural phase transition into a dimerized phase at low temperature accompanied by the opening of a spin gap [1]. This spin-Peierls transition was first observed in organic systems [2], but has found considerable experimental attention after its recent discovery in CuGeO_3 ($T_{sp} = 14$ K) [3]. The α' -phase of NaV_2O_5 appears to be the second inorganic compound where a similar transition was observed with an even higher transition temperature $T_{sp} = 34$ K [4]. The size of the spin gap determined by neutron scattering [5], susceptibility measurements [6] and several other techniques falls in the range 85–100 K. The transition into the low-temperature dimerized structure was confirmed by X-ray scattering [5], NMR [7], Raman scattering [6] and thermal-expansion [8] yet the detailed deformation pattern is still unknown. Recently phonons with anomalous broad line shape indicating a strong spin-phonon coupling even far above T_{sp} were found in Raman experiments [9]. These experiments also show new low energy excitations in the spin-Peierls phase, which either appear because of the lower symmetry or may reflect characteristic spin excitations of the dimerized spin chains, *e.g.* a soliton bound state at 64 cm^{-1} [9].

Based on an early structure determination for α' - NaV_2O_5 [10], the current picture for the origin of the one-dimensional magnetic properties rests on the assumption of charge discommensuration into V^{4+} and V^{5+} chains [4,5,7,9,11,12]. In Figure 1 the V1 and V2 chains in b -direction would correspond to these different charged vanadium chains. In this picture the V^{4+} chain would

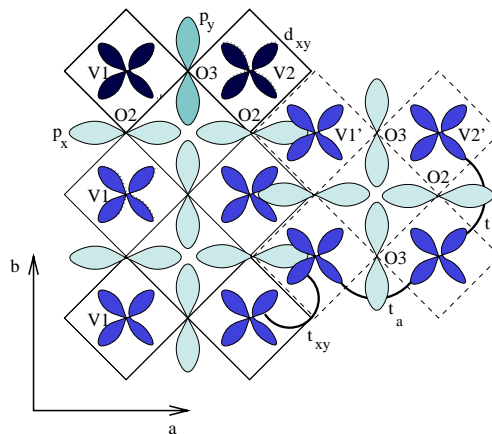


Fig. 1. Orbital structure of α' - NaV_2O_5 in the a - b plane. The lowest d -orbitals with d_{xy} -symmetry are occupied by one electron per two V-atoms. The O p -orbitals at the corners of square pyramids (where only the basal plane is indicated) are occupied, with energies ranging from -3 eV down to -7 eV relative to the chemical potential. Solid (dashed) squares indicate the downward (upward) orientation of the pyramids (for structural details see Refs. [4,13]). The d_{xy} orbitals have a direct overlap t_{xy} along the V2-V1'-V2-V1' zig-zag chain. The largest hopping matrix element t_a is, however, *via* double exchange interaction involving an O3 p_y orbital. The resulting bonding is manifested in the structure by the shortest planar V-O distance along the V1-O3-V2 bond.

correspond to a spin-1/2 Heisenberg chain. A problem with this picture is, however, the missing physical argument for such a strong charge modulation.

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In fact a recent new structural analysis of α' - NaV_2O_5 by von Schnering *et al.* [13] clearly shows that all vanadiums are equivalent and in a mixed valent state. Furthermore the charge-ordered state at room temperature was found to be in conflict with Raman scattering experiments [14]. Since there is one d -electron per two V ions an explanation for the insulating properties must be found which does not rest on charge discommensuration.

The aim of this work is to show how in such an intermediate valence situation correlation effects can lead to a quasi-1D Heisenberg antiferromagnet. An important structural information [13], which is crucial for our analysis, are the V–O distances d in the a – b plane (Fig. 1): $d(\text{V1–O3}) = d(\text{V2–O3}) = 1.825 \text{ \AA}$, $d(\text{V1–O2} \parallel b) = 1.916 \text{ \AA}$ and $d(\text{V1–O2} \parallel a) = 1.986 \text{ \AA}$. This implies that the V1–O3–V2 bond is much shorter than the V1–O2–V1 bond in b -direction. This additional bonding effect can be attributed to the d_{xy} -electrons. From Figure 1 we see that the d_{xy} -orbitals have a direct overlap in one direction, *e.g.* V2–V1', which is however quite small $t_{xy} \cong 0.3 \text{ eV}$ [15,16]. Yet a d_{xy} -electron can also hop between V1 and V2 *via* a double exchange like process. In such a process first an electron hops from the occupied O3 p_y -orbital to V2 with an excitation energy $\Delta\epsilon_y = \epsilon(d_{xy}) - \epsilon(p_y)$, and in a second step the V1-electron annihilates the oxygen hole. The matrixelement for this process is $t_a \cong t_{pd}^2/\Delta\epsilon_y$. The matrixelement t_{pd} depends on the vanadium-oxygen distance d and can be estimated with the help of Harrison's [16] solid state table as $t_{pd} = \eta_{pd\pi} \hbar^2 r_d^{3/2}/md^{7/2}$, where $\eta_{pd\pi} = 1.36$, $\hbar^2/m = 7.62 \text{ eV\AA}^2$, and $r_d = 0.98 \text{ \AA}$ for vanadium. This gives $t_{pd} \cong 1.2 \text{ eV}$. The p – d excitation energies are determined from a LMTO-bandstructure calculation [15], which yields $\Delta\epsilon_y \cong 4 \text{ eV}$ and $\Delta\epsilon_x \cong 6.5 \text{ eV}$, respectively. Hence $t_a \cong 0.35 \text{ eV}$, while the corresponding matrixelement $t_b \cong 0.15 \text{ eV}$ is considerably smaller because of the larger oxygen-vanadium distance and the larger $\Delta\epsilon_x$. We note that the larger value for t_a is consistent with the stronger bonding of the V1–O3–V2 bond.

The Hamiltonian for the d_{xy} -electrons may be written in terms of creation and density operators $d_{i\alpha\sigma}^\dagger$ and $n_{i\alpha\sigma} = d_{i\alpha\sigma}^\dagger d_{i\alpha\sigma}$, respectively, in the form

$$H_d = - \sum_{i\sigma} t_a (d_{i1\sigma}^\dagger d_{i2\sigma} + H.c.) + U_d \sum_{i\alpha} n_{i\alpha\uparrow} n_{i\alpha\downarrow} - \sum_{\langle ij \rangle \alpha \beta \sigma} t_{ij}^{\alpha\beta} (d_{i\alpha\sigma}^\dagger d_{j\beta\sigma} + H.c.), \quad (1)$$

where we have introduced a cell structure. Here a cell contains two vanadium atoms V1 and V2, *i.e.* $\alpha = 1$ and 2, and is labeled by a cell index $\mathbf{i} = (i_a, i_b)$. The cell-Hamiltonian consists of a kinetic energy term t_a and the local interaction $U_d \cong 4 \text{ eV}$ [17]. In H_d we dropped a shift of the single particle levels which is only relevant for total energy considerations [18]. The hopping between cells is defined by the last term, where

$$t_{ij}^{\alpha\beta} = \begin{cases} t_b & \text{for } \alpha = \beta, j_a = i_a, j_b = i_b \pm 1 \\ t_{xy} & \text{for } \alpha \neq \beta, j_a = i_a \pm 1, j_b = i_b \pm \frac{1}{2} \end{cases} \quad (2)$$

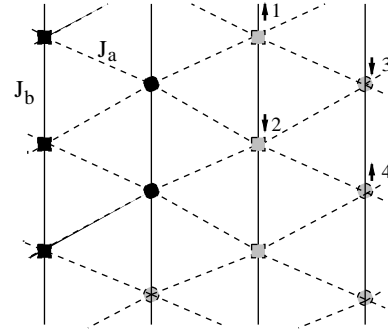


Fig. 2. Geometric structure of the effective spin model. A site corresponds to a V1–O3–V2 cell with a single d -electron. Dark symbols indicate the part of the structure shown in Figure 1. The largest antiferromagnetic interaction is J_b , while the frustrated interaction J_a between neighboring b -chains is small. The one-dimensional magnetic structure is further enhanced by the topology of the lattice. The antiferromagnetic interaction J_a of spin 3 with spins 1 and 2 on the neighbor chain is frustrated.

Since the ratios between U_d and the various hopping matrix elements are quite large, we are confronted with a strong correlation problem.

In the following we shall use a cell-perturbation method [19] based on the above cell structure, where each V1–V2 cell contains in the average a single d -electron. The advantage of the cell decomposition is the capability to treat the local correlations exactly. The complete set of states is then labeled by the quantum numbers of the cells, *i.e.* including the number of electrons within a cell. In the one electron sector the cell states are simply bonding and antibonding states at energies $\pm t_a$ and corresponding operators $b_{i\sigma}^\dagger$ ($a_{i\sigma}^\dagger$) = $\frac{1}{\sqrt{2}}(d_{i1\sigma}^\dagger \pm d_{i2\sigma}^\dagger)$, respectively. The low energy configurations $b_{i\sigma}^\dagger b_{j\sigma'}^\dagger$, of two electrons in neighbor cells \mathbf{i} and \mathbf{j} are coupled in second order due to the hopping t_{ij} . The intermediate states have two electrons in one cell. The low-energy singlet and triplet states have excitation energies $\Delta E_s = 2t_a - \frac{1}{2}(\sqrt{U_d^2 + 16t_a^2} - U_d)$ and $\Delta E_t = 2t_a$, respectively. Other singlet states are at much higher energy $E \geq U_d + 2t_a$. The Heitler-London singlet-triplet splitting of the low-energy intermediate states turns out to be crucial for the anisotropic nature of the magnetic properties.

The coupling of the $b_{i\sigma}^\dagger b_{j\sigma'}^\dagger$ configurations may be expressed in compact form by the spin-1/2 Hamiltonian

$$H = \sum_{\langle ij \rangle} [J_{ij}^s (\mathbf{S}_i \mathbf{S}_j - \frac{1}{4} n_i n_j) - J_{ij}^t (\mathbf{S}_i \mathbf{S}_j + \frac{3}{4} n_i n_j)], \quad (3)$$

where $\mathbf{S}_i = \frac{1}{2} b_{i,\sigma}^\dagger \boldsymbol{\tau}_{\sigma\sigma'} b_{i,\sigma}$ defines the spin of bonding electrons in terms of the vector of Pauli spin matrices $\boldsymbol{\tau}$ and $n_i = \sum_{\sigma} b_{i,\sigma}^\dagger b_{i,\sigma}$ their density. Here J_{ij}^s and J_{ij}^t denote the coupling of neighboring cells in the singlet- and triplet channel, respectively. The relative size of the exchange integrals is strongly influenced by the geometrical structure (Figs. 1 and 2). The coupling of cells in a -direction, *i.e.* *via* t_{xy} , yields $J_a^s = 2(t_{xy}/2)^2/\Delta E_s$ and $J_a^t = 2(t_{xy}/2)^2/\Delta E_t$.

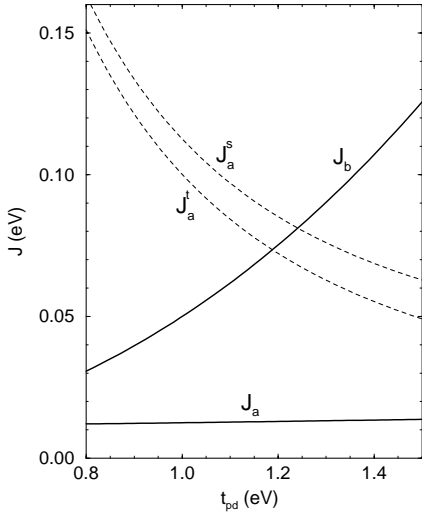


Fig. 3. AF-exchange coupling between d -electrons in nearest neighbor $V1-O3-V2$ bonds as function of t_{pd} : (a) J_b along b -direction (solid line), (b) the small coupling $J_a = J_a^s - J_a^t$ between different b -chains mediated by $t_{xy} \sim 0.3$ eV results from the cancellation of the contributions J_a^s and J_a^t from the Heitler-London split singlet and triplet intermediate states (dashed lines).

They differ only because of the singlet-triplet splitting $E_{s-t} = \frac{1}{2}(\sqrt{U_d^2 + 16t_a^2} - U_d)$. The coupling of cells in b -direction is $J_b^s = 2t_b^2/\Delta E_s$ and $J_b^t = 0$, where the latter exchange integral vanishes due to symmetry. This has the effect that the total exchange constants in $H = \sum J_{ij}\mathbf{S}_i\mathbf{S}_j$ almost cancel along a -direction, *i.e.* $J_a = J_a^s - J_a^t$, whereas along the ‘ b -chains’ $J_b = J_b^s$ there is no such reduction. These estimates are valid if the ratios $\frac{2t_a}{U}$ and $\frac{t'}{2t_a}$, with $t' = \{t_b, t_{xy}/2\}$, are small compared to 1. Numerical estimates for these exchange integrals based on degenerate perturbation theory are shown in Figure 3 as function of the vanadium-oxygen ($V1-O3$) hybridization t_{pd} . For the estimated value $t_{pd} \simeq 1.2$ eV one finds $J_b \simeq 75$ meV and $J_a \simeq 13$ meV.

Experimental estimates for the exchange constants are usually obtained from the position of the maximum of the uniform susceptibility $\chi(T)$. In the following we study the effect of the interchain coupling J_a and the thereby introduced frustration of the spin-1/2 model (3) using a finite temperature diagonalization technique [20]. The geometrical structure of the lattice (Fig. 2) is similar to the resonating valence bond systems studied by Anderson and Fazekas [21]. Results for a two-leg ladder (‘railroad-trestle’) with periodic boundary conditions along a - and b -direction and different interchain coupling strength J_a/J_b are shown in Figures 4 and 5. Since the interchain coupling is frustrated the change of $\chi(T)$ is relatively small. The maximum of $\chi(T)$ is at the temperature $T_\chi^{max} = a_\chi J_b$, where $a_\chi = 0.8$ for a 2×12 system in the absence of the interchain coupling, *i.e.* $J_a/J_b = 0$. The exact result for the thermodynamic limit recently obtained by Eggert *et al.* [22] using the thermal Bethe ansatz is $a_\chi = 0.6$. Interchain coupling leads to a small shift of the maxi-

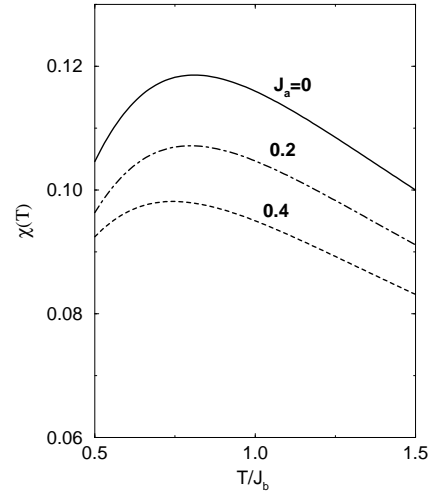


Fig. 4. Uniform susceptibility $\chi(T)$ (in units of $1/J_b$) for a two-leg ladder (2×12) with the structure given in Figure 2 for different interchain coupling strength $J_a/J_b = 0, 0.2$ and 0.4 and periodic boundary conditions.

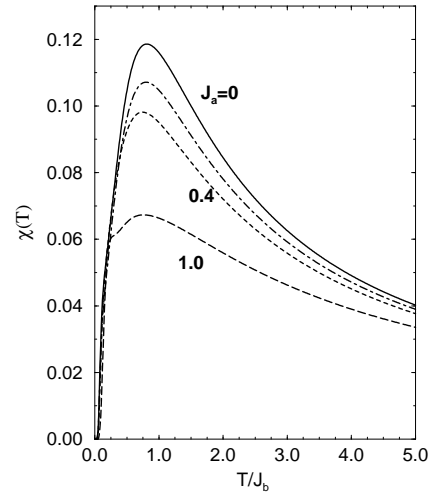


Fig. 5. Uniform susceptibility $\chi(T)$ for a 2×12 two-leg ladder for different interchain coupling strength $J_a/J_b = 0, 0.2, 0.4$ and 1.0 on a large temperature scale. The rapid drop below $T/J_b \leq 0.2$ is a finite size effect.

mum by about 2% to lower temperatures for the value $J_a/J_b \sim 0.2$ estimated above (Fig. 4).

We note that lattice fluctuations are expected to lead to a further weakening of antiferromagnetism and an additional shift of the maximum of $\chi(T)$ to lower T . A recent study of this effect by Sandvik *et al.* [23] shows that this may lead to a reduction of T_χ^{max} by 15% for a one-dimensional Heisenberg chain. Combining these two effects one arrives at the estimate $a_\chi^{tot} \sim 0.50$. From the susceptibility measurements [4,11] for α' - NaV_2O_5 one finds $T_\chi^{max} \sim 350$ K, which leads to the estimate $J_b^{exp} \sim 700$ K. This is in reasonable agreement with the theoretical value $J_b \sim 75$ meV derived in this work. In view of the simplicity of the model and the rough estimates of the parameters this is quite satisfactory.

We briefly comment on the band picture, *i.e.* ignoring the effect of electron correlations. Since double-exchange is not contained in this scheme, the only large hopping matrix element is t_{xy} . This leads to two degenerate one-dimensional d_{xy} -bands from the zig-zag chains $V2-V1'-V2-V1'$ and $V2'-V1-V2'-V1$ (Fig. 1), respectively, since there are two zig-zag b -chains per unit cell. Each band is quarter-filled and one may expect a usual Peierls transition to occur due to an appropriate modulation of the structure in b -direction. Although this could explain the insulating properties at room temperature, such an explanation is obviously incorrect, since it would rule out a spin-Peierls transition at low temperature. Of course the large ratio U_d/t_{xy} already excludes the straightforward application of the band picture. Nevertheless for sufficiently large t_{xy} one expects that the correlated band picture applies. Estimates of the ground state energies for the localized regime and the band picture suggest that this is the case for $t_{xy} > 1.5t_a$.

The bands obtained by a real bandstructure calculation deviate from this idealistic picture due to small interchain couplings, which is also reflected in shorter $V1-O3-V2$ bonds [15]. The full bandstructure calculation predicts a metallic state.

We remark that photoemission experiments in combination with XAS would provide a sensitive test of the present picture, since the lowest unoccupied states are the singlet and triplet states, while higher lying ‘two-particle’ states are split by U_d . Optical conductivity measurements on the other hand should show a relatively small ‘single particle’ gap $E_g \cong 2t_a$.

In summary we have shown that α' - NaV_2O_5 is an insulator due to strong correlations, *i.e.* large U_d . However since the single electron orbitals have bonding character, *i.e.* involving two V-atoms, the magnetic structure is induced *via* 2-electron molecular singlet and triplet states which are Heitler-London split. Due to the almost perfect cancellation of the triplet- and singlet-interactions in a -direction the spin system is essentially one-dimensional. We stress that doubly occupied states with energy $\sim U_d$, which usually contribute to the magnetic interaction in Mott-Hubbard insulators, have little influence since they are at much higher energy. Therefore we propose the name *Heitler-London insulator* as a more precise characterization for such systems.

Note added in proofs

Recent optical measurements by Golubchik *et al.* [24] show a pronounced polarization dependence and an optical gap $E_g \sim 0.6-0.7$ eV consistent with our results. The next higher excitation band with onset at $\omega \sim 3.5$ eV falls in the range of the $p-d$ interband transitions. A similar conclusion about the structure of α' - NaV_2O_5 as in reference [13] was obtained independently by Smolinski *et al.* [25]. Their theoretical interpretation of NaV_2O_5 as a quarter-filled ladder compound is, however, largely based on very small inter-ladder hopping matrix elements t_1 and

t_2 , which distinguishes their analysis from the one presented here.

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