A new view of the electronic structure of the spin-Peierls compound $\alpha'$-NaV$_2$O$_5$

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Abstract. The present understanding of the electronic and magnetic properties of $\alpha'$-NaV$_2$O$_5$ 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 small.

Dedicated to J. Zittartz on the occasion of his 60th birthday

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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$_3$ ($T_{sp} = 14K$)[3]. The $\alpha'$-phase of NaV$_2$O$_5$ appears to be the second inorganic compound where a similar transition was observed with an even higher transition temperature $T_{sp} = 34K$[4]. The size of the spin gap was determined by neutron scattering[5], Raman[6] and other experiments. The transition into the low-temperature dimerized structure was confirmed by X-ray scattering[4], NMR[7], thermal-expansion[8] yet the detailed deformation pattern is still unknown.

Based on an early structure determination for $\alpha'$-NaV$_2$O$_5$[9], 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][10]. In Fig.1 the V1 and V2 chains in b-direction would corre-
spond to these different charged vanadium chains. In this picture the V$^{4+}$ chain would 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.

In fact a recent new structural analysis of α$'$-NaV$_2$O$_5$ by von Schnering et al.[12] 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[13]. 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[12], which is crucial for our analysis, are the V-O distances $d$ in the a-b plane (Fig.1): $d$(V1-O3)=$d$(V2-O3)=1.825 Å, $d$(V1-O2||b)=$d$(V1-O2||a)=1.916 Å and $d$(V1-O2∥a)=1.986 Å. 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 Fig. 1 we see that 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.

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The $p_d$ excitation energies are determined from a LMTO-bandstructure calculation[14], which yields $\Delta \epsilon_y \cong 4$ eV.

**Fig. 1.** Orbital structure of α$'$-NaV$_2$O$_5$ 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. Solid (dashed) squares indicate the downward (upward) orientation of the pyramids (for structural details see Refs.[12] and [4]). 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.
and $\Delta \epsilon_x \cong 6.5$ eV, respectively. Hence $t_a \cong 0.35$ eV, while the corresponding matrix element $t_b \cong 0.15$ 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

$$H_d = -\sum_{i\sigma} t_{a}(d_{1i\sigma}^\dagger d_{2i\sigma} + H.c.) + U_d \sum_{i\alpha} n_{1i\alpha\uparrow} n_{1i\alpha\downarrow}$$

$$-\sum_{(ij)} t_{ij}(d_{i\alpha\sigma}^\dagger d_{j\beta\sigma} + H.c.),$$

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 $i = (i_a, i_b)$. The cell-Hamiltonian consists of a kinetic energy term $t_a$ and the local interaction $U_d \cong 4$ eV[18]. In $H_d$ we dropped a shift of the single particle levels which is only relevant for total energy considerations[17]. The hopping between cells 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 $b_{i\alpha\sigma}^\dagger (a_{i\alpha\sigma}^\dagger) = \frac{1}{\sqrt{2}}(d_{i1\sigma}^\dagger \pm d_{i1\sigma}^\dagger)$, respectively. The low energy configurations $b_{i\alpha\sigma}^\dagger b_{j\beta\sigma}^\dagger$ of two electrons in neighbor cells $i$ and $j$ 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 $\Delta E_s = 2 t_a - \frac{1}{2}(\sqrt{U_d^2 + 16t_a^2} - U_d)$ and $\Delta E_t = 2 t_a$, respectively. Other singlet states are at much higher en-
ergy $E \geq U_d + 2t_a$. 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 $b^\dagger_\sigma b^\dagger_{\sigma'}$ configurations may be expressed in compact form by the spin-$1/2$ Hamiltonian

$$H = \sum_{\langle ij \rangle} \left[ J^s_{ij} (S_i S_j - \frac{1}{4} n_i n_j) - J^t_{ij} (S_i S_j + \frac{3}{4} n_i n_j) \right],$$

(3)

where $S_i = \frac{1}{2} b^\dagger_{i,\sigma} \tau_{\sigma\sigma'} b^\dagger_{i,\sigma'}$ defines the spin of bonding electrons in terms of the vector of Pauli spin matrices $\tau$ and $n_i = \sum_\sigma b^\dagger_{i,\sigma} b_{i,\sigma}$ their density. Here $J^s_{ij}$ and $J^t_{ij}$ 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 (Fig. 1 and 2). The coupling of cells in a-direction, i.e. via $t_{xy}$, yields $J^s_a = 2(t_{xy}/2)^2/\Delta E_s$ and $J^t_a = 2(t_{xy}/2)^2/\Delta E_t$. They differ only because of the singlet-triplet splitting $E_s - t = \frac{1}{2}(\sqrt{U^2_d + 16t^2_a} - U_d)$. The coupling of cells in b-direction is $J^s_b = 2t^2_b/\Delta E_s$ and $J^t_b = 0$, where the latter exchange integral vanishes due to symmetry. This has the effect that the total exchange constants in $H = \sum J_{ij} S_i S_j$ almost cancel along a-direction, i.e. $J_a = J^s_a - J^t_a$, whereas along the ‘b-chains’ $J_b = J^s_b$ there is no such reduction.

These estimates are valid if the ratios $\frac{2t_a}{U_d}$ and $\frac{t_{xy}}{4t_a}$, 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 Fig. 3 as function of the vanadium-oxygen (V1-O3) hybridization $t_{pd}$. For the estimated value $t_{pd} \approx 1.2$ eV one finds $J_b \approx 75$ meV and $J_a \approx 13$ 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[19]. The geometrical structure of the lattice (Fig. 2) is similar to the resonating valence bond systems studied by Anderson and Fazekas[20]. Results for a two-leg ladder (‘railroad-trestle’) with periodic boundary conditions along a- and b-
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Fig. 4. Uniform susceptibility \( \chi(T) \) for a two-leg ladder \((2 \times 12)\) with the structure given in Fig. 2 for different interchain coupling strength \( J_a/J_b \) = 0, 0.2 and 0.4 and periodic boundary conditions.

direction and different interchain coupling strength \( J_a/J_b \) are shown in Fig. 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 \( T_{\chi}^{\text{max}} = a_\chi J_b \), where \( a_\chi = 0.8 \) for a \( 2 \times 12 \) 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 \textit{et al.} [21] using the thermal Bethe ansatz is \( a_\chi = 0.6 \). Interchain coupling leads to a small shift of the maximum 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 \textit{et al.} [22] shows that this may lead to a reduction of \( T_{\chi}^{\text{max}} \) by 15% for a one-dimensional Heisenberg chain. Combining these two effects one arrives at the estimate \( a_\chi^{\text{tot}} \sim 0.50 \). From the susceptibility measurements [4,10] for \( \alpha\)'-NaV\(_2\)O\(_5\) one finds \( T_{\chi}^{\text{max}} \sim 350 \) 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 dimerization 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\[14\]. 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 of order \(2t_a\).

In summary we have shown that \(\alpha'\)-NaV\(_2\)O\(_5\) 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 suggest the name Heitler-London insulator as a more precise characterization for such systems.

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