NaV$_2$O$_5$ as an Anisotropic $t$--$J$ Ladder at Quarter Filling

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Based on recent experimental evidences that the electronic charge degrees of freedom plays an essential role in the spin-Peierls-like phase transition of NaV$_2$O$_5$, we first make the mapping of low-energy electronic states of the $d$--$p$ model for NaV$_2$O$_5$ to the quarter-filled $t$--$J$ ladder with anisotropic parameter values between legs and rungs, and then show that this anisotropic $t$--$J$ ladder is in the Mott insulating state, of which lowest-energy states can be modeled by the one-dimensional Heisenberg antiferromagnet with the effective exchange interaction $J_{\text{eff}}$ whose value is consistent with experimental estimates. We furthermore examine the coupling between the ladders as the trellis lattice model and show that the nearest-neighbor Coulomb repulsion on the zigzag-chain bonds can lead to the instability in the charge degrees of freedom of the ladders.

KEYWORDS: NaV$_2$O$_5$, spin-Peierls transition, $t$--$J$ ladder, quarter filling, $d$--$p$ model, trellis lattice

Recently it has been reported\cite{1} that the phase transition at $T_c = 34$ K in NaV$_2$O$_5$ is not a conventional spin-Peierls transition but rather a charge ordering into a geometrical configuration of charges with the spin excitation gap. Although there are still a lot of controversies in experimental data,\cite{2,3} this work certainly casts doubt on the present understanding of the basic electronic states of this system; i.e., electronic charge degrees of freedom cannot be eliminated in the low-energy physics of the system. More specifically, we might have to start from a quarter-filled ladder-type model, rather than from the one-dimensional (1D) Heisenberg model with only the dimerizing lattice degrees of freedom, to discuss this phase transition.

In this paper we consider this unconventional spin-Peierls system. We first analyze the low-energy states of the $d$--$p$ model by using a V$_2$O$_4$ cluster and by making one-to-one correspondence of the states to analytically solved states of the 4-site $t$--$J$ cluster we derive the anisotropic $t$--$J$ ladder Hamiltonian which we argue can hopefully be a starting model for the low-energy physics of this system. We will show that the mapping works quite well and enables us to evaluate the parameter values for the Hamiltonian. A Lanczos diagonalization technique is then applied to the finite-size clusters of this ladder model to examine its low-energy states. We will thereby show that our anisotropic $t$--$J$ ladder has a finite charge gap in the realistic parameter region and the lowest-energy levels can be modeled by the 1D Heisenberg antiferromagnet with the effective exchange interaction consistent with experimental estimates. We will moreover argue that because the model still has the charge degrees of freedom in its low-energy sector it can be a starting Hamiltonian for describing the unconventional spin-Peierls system NaV$_2$O$_5$ if appropriate lattice degrees of freedom and/or some presently unknown factors are taken into account; we will suggest a possible scenario that a fairly small inter-ladder repulsive interaction can induce instability for the charge disproportionation in the ladders.

High-energy physics of the system may be contained in a $d$--$p$ model cluster V$_2$O$_4$ (a pair of the rungs) which is illustrated in Fig. 1. The $d$--$p$ Hamiltonian reads

$$H_{d-p} = - \sum_{i \sigma} (\pm) d^{\dagger}_{i \sigma} p_{i \sigma} + \text{H.c.} + U_d \sum_i n^{d^\dagger}_i n^{d^\dagger}_{i+1} + \sum_i \varepsilon^{d^\dagger} n^d_i + \sum_i \varepsilon^{p^\dagger} n^p_i \quad (0.1)$$

where $d^{\dagger}_{i \sigma}$ ($p_{i \sigma}$) creates (annihilates) a spin-$\sigma$ electron on the $d_{xy}$-orbital at site $i$ (neighboring $p$-orbital at site $i$), and $n^{d^\dagger}_{i \sigma}$ and $n^{p^\dagger}_{i \sigma}$ are the electron number operator. We take into account (i) the hopping parameters $t_{pd}$ between the $d_{xy}$-orbital on V ion and the $p_x$-orbital ($t^x_{pd}$) and $p_y$-orbital ($t^y_{pd}$) on the neighboring O ions where the phase factor $\langle \pm \rangle$ has to be taken appropriately, (ii) energy-level difference $\Delta_{pd} = \varepsilon^d_i - \varepsilon^p_i$ between the $d_{xy}$-orbital and the $p_x$-orbital ($\Delta^x_{pd}$) and $p_y$-orbital ($\Delta^y_{pd}$), and (iii) Coulomb repulsion $U_d$ on V ions. The anisotropy of the parameter values will turn out to be important. We note that this cluster is the smallest one in that it takes into account the anisotropic legs and rungs simultaneously; i.e., it contains the effective repulsive interaction on the rungs which can lead to the charge gap, the effective exchange interaction between the rungs which can lead to the 1D Heisenberg antiferromagnet, and the exchange interaction between the neighboring V ions on the leg of the ladder which can lead to the spin gap when the system is dimerized at $T < T_c$. The coupling between ladders is neglected for the moment (see below for this effect). Values of the $d$--$p$ model parameters are taken from Ref.\cite{1}: $t^x_{pd}$ and $t^y_{pd}$ take the value of 1.22 and 1.03 eV, respectively, but are assumed to depend on the bond length $d$ as $t_{pd} \propto d^{-7/2}$. $\Delta^x_{pd} = 6.5$ eV, $\Delta^y_{pd} = 4$ eV, and $U_d = 4$ eV. There are 10 electrons in the cluster.
Energies of several low-lying states of the V$_4$O$_4$ cluster are evaluated by a Lanczos diagonalization method and are compared with the analytically solved low-energy states of the 4-site t–J cluster with two electrons. The t–J Hamiltonian reads

$$H_{t–J} = - \sum_{\langle ij \rangle \sigma} t_{ij} (c_{i\sigma}^\dagger c_{j\sigma} + \text{H.c.}) + \sum_{\langle ij \rangle} J_{ij} (\mathbf{S}_i \cdot \mathbf{S}_j - \frac{1}{4} n_i n_j)$$

(0.2)

where $\langle ij \rangle$ represents the nearest-neighbor bonds along the legs and rungs with the hopping and exchange parameters $t_{ij}$ and $J_{ij}$ taking $t_\perp$ and $J_\perp$ for the rungs and $t_\parallel$ and $J_\parallel$ for the legs. $c_{i\sigma}^\dagger = c_{i\sigma}(1 - n_{i\sigma})$ is the constrained electron-creation operator at site $i$ and spin $\sigma (= \uparrow, \downarrow)$. $\mathbf{S}_i$ is the spin-$\frac{1}{2}$ operator, and $n_i = n_{i\uparrow} + n_{i\downarrow}$ is the electron-number operator. We confirm that the several low-lying states of both $d$–$p$ and $t$–$J$ clusters have the same quantum numbers and characters and thus we find that the mapping is straightforward. Here we determine the values of the 4 ladder-parameters by fitting the energies of the lowest 5 states for the $d$–$p$ and $t$–$J$ clusters (the extra one is for the origin of energy). The obtained values of the ladder parameters for the realistic bond lengths are: $t_\perp = 0.298$, $t_\parallel = 0.140$, $J_\perp = 0.049$, and $J_\parallel = 0.029$ in units of eV (which we will use in the following discussions unless otherwise indicated). In Fig. 2, we show the bond-length dependence of these parameters. We note that with increasing $d_\parallel$, the value of $J_\parallel$ decreases as expected, but the value $J_\perp$ also decreases considerably. Also noted is that with increasing $d_\perp$ the value of $J_\perp$ increases. These are from the higher-order contributions to the exchange interactions. The hopping parameters $t_\perp$ and $t_\parallel$ on the other hand vary more or less as expected.

The single-particle spectra from the quarter-filled ground states of the V$_4$O$_4$ cluster and corresponding t–J cluster are shown in Fig. 3. We find a very good agreement, demonstrating that the mapping is satisfactory also for the one-electron added and one-electron removed sectors of the cluster Hilbert space.

Now let us examine the electronic states of the obtained anisotropic t–J ladder at quarter filling. Here we examine the charge gap $\Delta_c$ of the model, which is not yet well known although there were some discussions. The charge gap is defined by

$$\Delta_c = \frac{1}{2} \left[ \left[ E_0(N_\uparrow + 1, N_\downarrow) - E_0(N_\uparrow, N_\downarrow) \right] - \left[ E_0(N_\uparrow, N_\downarrow) - E_0(N_\uparrow - 1, N_\downarrow) \right] \right]$$

(0.3)

where $E_0(N_\uparrow, N_\downarrow)$ is the ground-state energy of the system with $N_\uparrow$ up-spin and $N_\downarrow$ down-spin electrons. This is evaluated for 8, 12, and 16-site clusters with either periodic or antiperiodic boundary condition to minimize the shell effect on the values of $\Delta_c$. The results are plotted in Fig. 4 as a function of $1/L$ ($L$ is the length of the ladder) to see the value at the infinite system size. We find that at least for $t_\perp/t_\parallel \gtrsim 1.3$–1.5 the gap opens up although the situation is still unclear for $t_\perp \approx t_\parallel$ in the present calculations of small finite-size systems. We also calculate the equal-time charge correlation function $\langle n_i n_j \rangle$ and find that the probability of finding two electrons on the same rung is very small for $t_\perp/t_\parallel \gtrsim 1.3$, indicating that one electron is localized on each rung. It seems thus quite reasonable to say that the anisotropic ladder at quarter filling is in the insulating state for the realistic parameter values.

The mechanism of this charge localization is common in a class of quarter-filled organic systems where the Mott insulating phase is realized due to dimerization: with increasing dimerization strength a dimer turns into...
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Fig. 3. Single-particle spectra for the $d$–$p$ cluster compared with those of the $t$–$J$ cluster at quarter filling. The spectra near the chemical potential (set at $\omega = 0$) are enlarged in the lower panel. For the $d$–$p$ model, the total spectra summing up the contributions from the V $d_{xy}$-orbital and O $p_x$- and $p_y$-orbitals are shown although around the chemical potential the spectral weight is almost completely from the V $d_{xy}$-orbital.

Fig. 4. Charge gap $\Delta_c/t_{\parallel}$ of the finite-size clusters for the quarter-filled $t$–$J$ ladder as a function of the inverse of the cluster size $1/L$. Anisotropy in the hopping parameters $t_{\perp}/t_{\parallel}$ is varied with keeping $J_{\perp}/J_{\parallel} = 2$ and $J_{\parallel}/t_{\perp} = 0.2$ constant.

an effective single site of a half-filled antibonding state with Hubbard-like repulsive interaction. This mechanism operates also in the anisotropic ladder at quarter filling if we can regard the rung as a dimer, and actually in some parameter region, we do have this insulating phase as we have seen above. This Mott insulating phase can be modeled as a 1D Heisenberg antiferromagnet of which the effective exchange interaction is estimated to be $J_{\text{eff}} = 85$ meV from the singlet-triplet splitting in the 4-site $t$–$J$ cluster. This value is consistent with the value obtained in Ref.11 and should also be consistent with values determined from the observed temperature dependence of the uniform susceptibility $\chi(T)$ if a small inter-chain exchange coupling and some other effects are taken into account.1 Note that the value of $J_{\parallel}$ is much smaller than the value of $J_{\text{eff}}$ (see Fig. 3); the picture that the electrons order on one of the legs of the ladder already above $T_c$ should predict a very different peak position in $\chi(T)$. Also noted is that the bond-length dependence of $J_{\text{eff}}$ is very strong and anisotropic (see Fig. 3), which may be confirmed by some high-pressure experiment. The resultant picture for the high-temperature phase of NaV$_2$O$_5$ is thus equivalent to that of Horsch and Mack3 although the procedure of derivation of the 1D Heisenberg model is quite different.

In the real materials, we have to take into account the coupling between the ladders, i.e., the system may be the one modeled as a two-dimensional (2D) trellis lattice (ladders connected with zigzag chain bonds as in Fig. 1 (b)). We examine the electronic states, i.e., the equal-time charge correlation function and charge gap for the 16-site clusters of this lattice (or coupled two $4 \times 2$ ladders), and find that the basic electronic state that one electron is localized on each rung is maintained against the inter-ladder hopping integral of up to $t_{xy} \simeq 1.2t_{\parallel}$. The reported values of $t_{xy}$ are fairly small, so that the electronic state of the real materials may be in this localization regime. We however immediately notice that it seems unlikely that the $t$–$J$ ladder with the small $J/t$ values has inherent charge instability in itself even though it is anisotropic; the only possibility seems to be the phase separation realized for very large $J_{\parallel}$ values where the electrons are localized on one of the legs to form a Heisenberg chain.

The simplest interaction that can lead to the charge instability is the intersite Coulomb repulsion. In (TMTTF)$_2$X, e.g., the nearest-neighbor Coulomb repulsion is discussed to be the origin of the observed charge disproportionation. Here we introduce the repulsive interaction $V$ between ladders, i.e., on the zigzag chain bonds running along the crystallographic $b$-axis, which have the shortest bond-length among V-V bonds. We use the two $4 \times 2$-ladder clusters for modeling the trellis lattice and calculate the charge correlation function $\langle n_i n_{i+1} \rangle$. As shown in Fig. 5, the tendency to the charge disproportionation where the electrons are localized on
one side of the legs is actually found for not too large values of $V$ (only $10$–$20\%$ of $U_d$). Once the 1D Heisenberg chain on one of the legs of the ladder is thus realized (by some phase transition in the thermodynamic limit) the system may be subject to the lattice dimerization which leads to the opening of the spin excitation gap.

An optimistic speculation for the phase transition of NaV$_2$O$_5$ is a realization of this charge ordering. In this picture, the critical temperature of the charge ordering needs not be the same as the spin-Peierls transition temperature of the spin chain of one of the legs of the ladder; if the former temperature is higher than the latter, we should observe two transitions independently. However, the opposite seems to be the case in real materials: when the ratio of the values of two hopping parameters deviates from $1$, which is suggestive to the observed second-order–like phase transition of NaV$_2$O$_5$, However, to decide if the mechanism suggested above really applies, we of course have to know much about the electronic states of this system from further experimental studies.

In summary, we have studied the electronic states of NaV$_2$O$_5$ by making the mapping of low-energy electronic states of the $d$–$p$ model for this compound to the quarter-filled $t$–$J$ ladder with anisotropic parameter values between legs and rungs. We have shown that this anisotropic $t$–$J$ ladder is in the Mott insulating state, of which lowest-energy states can be modeled by the one-dimensional Heisenberg chain with the effective exchange interaction $J_{\text{eff}}$ whose value is consistent with experimental estimates. We have also studied the coupling between the ladders by using the trellis lattice model and have shown that the intersite Coulomb repulsion on the zigzag-chain bonds can leads to the instability in the charge degrees of freedom of the ladders. A possible mechanism of the spin-Peierls–like phase transition of NaV$_2$O$_5$ has thereby been suggested.

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