Theoretical study of the optical conductivity of $\alpha'$-NaV$_2$O$_5$

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Using finite temperature diagonalization techniques it is shown that the quarter-filled $t$-$J$-$V$ model on a trellis lattice structure provides a quantitative explanation of the highly anisotropic optical conductivity of the $\alpha'$-NaV$_2$O$_5$ compound. The combined effects of the short-range Coulomb interaction and valence fluctuations of V-ions determine the main absorption and the fundamental gap. Inter-ladder hopping is necessary for the explanation of the anomalous in-gap absorption and generation of spectral weight at high energy. The role of valence fluctuations is explained in terms of the domain wall excitations of an anisotropic 2D Ising model in a transverse field close to criticality.

The physical properties of low dimensional quantum systems received considerable attention from both theoretical and experimental sides because of their unconventional spin and charge excitation spectra. In this respect, the vanadate $\alpha'$-NaV$_2$O$_5$, initially identified as an inorganic spin-Peierls (SP) compound, similar to CuGeO$_3$, has attracted great interest as a ladder system at quarter filling. The original X-ray structure analysis was pointing in favor of a non-centrosymmetric structure, implying two inequivalent vanadium sites. Hence, it was concluded that magnetic spin-1/2 V$^{4+}$ ions were forming one-dimensional (1D) chains well separated by nonmagnetic V$^{5+}$ chains in the $(a,b)$-plane. Based on this view the insulating properties appear natural, and various theoretical studies were performed using dimerized Heisenberg chains or spin-phonon models, which provided satisfactory results, e.g. for the susceptibility.

However, recent structure studies at room temperature showed that the V-ions are all equivalent with valence 4.5, which came as a surprise in view of the insulating properties of this substance. This puzzle was resolved by realizing that the molecular orbital state on a rung occupied by one electron is a key element of the electronic structure. In combination with the large local repulsion $U$, which confines the formal charges of V-ions to +4 and +5, respectively, the insulating behavior and the quasi-1D magnetic properties could be explained.

Surprisingly recent NMR-studies revealed the appearance of two different V-sites below the structural transition at $T_c = 34$ K, which clearly indicates that the transition is not of spin-Peierls type but rather driven by charge ordering. There have been several further experiments showing anomalous features compared to the usual spin-Peierls transition. The ratio between spin gap and transition temperature $2\Delta/k_B T_c \sim 6.5$ is much larger than the BCS mean-field value 3.92. The changes at $T_c$ of the dielectric constant and the thermal conductivity differ significantly from the case of CuGeO$_3$.

Moreover the magnetic field dependence $\Delta T_c \propto H^2$ is only about 20% of what is expected for a spin-Peierls transition.

Subsequently several theoretical papers analyzed the role of nearest and further neighbor Coulomb interaction, proposing zig-zag or linear charge order in the ground state. The nature of the excitation spectra of such a charge ordered singlet ground state is an open question. A test of these concepts could emerge from the very distinct experimental optical conductivity data. These experiments show quite different optical interband transitions for $a$- and $b$-polarization, i.e., reflecting the anisotropic structure of VO-layers. In addition to the larger spectral weight observed for $a$-polarization, the $\sigma^+$ spectra show weak low energy in-gap absorption.

We study the optical response assuming that the dynamics of electrons is described by an extended $t$-$J$-$V$ model including intra- and inter-rung Coulomb repulsion for a 2D system with trellis topology shown in Fig. 1. While in a previous numerical study zig-zag order was imposed, our results show that the excitation spectra are not only determined by the interladder coupling but also by strong intra-ladder valence fluctuations.

Our study suggests that $\alpha'$-NaV$_2$O$_5$ is close to a quantum critical point. The $t$-$J$-$V$ model is given by:

$$H = \sum_{\langle i,j \rangle,\sigma} t_{ij} (\hat{c}_{i,\sigma}^\dagger \hat{c}_{j,\sigma} + H.c.) + \sum_{\langle i,j \rangle} J_{ij} (\mathbf{S}_i \cdot \mathbf{S}_j - \frac{1}{4} n_i n_j) + \sum_{\langle i,j \rangle} V_{ij} n_i n_j \quad (1)$$

where $\hat{c}_{i,\sigma}^\dagger = \hat{c}_{i,-\sigma} (1 - n_{i,-\sigma})$ are constrained electron creation operators, $n_i = \sum_{\sigma} \hat{c}_{i,\sigma}^\dagger \hat{c}_{i,\sigma}$, and $\mathbf{S}_i$ is the spin-$\frac{1}{2}$ operator. The sums are over all bonds $(i,j)$ between neighbors on the trellis lattice and spin $\sigma = \uparrow, \downarrow$. The various hopping parameters $t_{ij}$, intersite Coulomb interactions $V_{ij}$, and exchange interactions $J_{ij}$ between vanadium neighbors are defined in Fig. 1. The exchange term is parametrized as $J_{ij} = 4t_{ij}^2 / U$, where $U$ is the corresponding on-site Hubbard interaction and we as-
sume that $U = 4.0$ eV. The calculation of $\sigma(\omega)$ has been performed by means of a generalization of the Lanczos technique for finite temperature (FTLM) \[23\]. In this approach the trace of the thermodynamic expectation value is evaluated by Monte-Carlo sampling, while for the evaluation of the relevant matrix elements the Lanczos method is used. Since the system is in an insulating state, one can restrict the calculation of $\sigma(\omega)$ to the finite frequency response given by the Kubo formula

$$\sigma_{m}(\omega) = \frac{1 - e^{-\beta\omega}}{\omega} Re \int_{0}^{\infty} d\tau e^{i\omega\tau} \langle j_{m}(\tau) j_{m} \rangle,$$

where $\beta = 1/k_{B}T$ and $j_{m}$ with $m(=a,b)$ denoting a component of the current operator

$$j_{m} = i \sum_{(i,j),\sigma} t_{ij} \cdot R_{m}^{ij}(\hat{c}_{i,\sigma}^\dagger \hat{c}_{j,\sigma} - H.c.).$$

Here $R_{m}^{ij}$ is the $m$-th component of the vector connecting neighboring sites $i$ and $j$.

First we consider the optical spectra for a system of ladders coupled only by the interaction $V_{xy}$, i.e., putting $t_{xy} = 0$. In Fig. 2 we compare results for spectra with polarization along $a$ and $b$ direction, respectively, for a cluster formed by two ladders whose size is shown in Fig. 1. Periodic boundary conditions are chosen. We use $t_{a} = 0.4$ and $t_{b} = 0.2$ eV. For the Coulomb repulsion we consider the symmetric condition $V_{a} = V_{b} = V$ \[11\] with $V = 0.8$ eV and vary $V_{xy}$. The $a$-spectra show a strong downward shift when increasing the value of $V_{xy}$, whereas the $b$-spectra hardly change. This behavior reflects the different nature of excited states relevant for $a$- and $b$-polarization. Polarization along $b$ connects to excitations with two and zero electrons per rung, respectively. The dynamics of these ‘doubles’ and ‘holons’ is not much influenced by valence fluctuations, since these rungs are fully occupied or empty, and also not by $V_{xy}$, since the interaction is frustrated (Fig. 1). The non-trivial $V_{xy}$ dependence of the $a$-spectra will be discussed below. Here we only emphasize that the $a$-spectra are sensitive to the ratio $2t_{a}/V_{b}$. Indeed, as one can see in Fig. 3, if valence fluctuations are weak (small $t_{a}$), the main weight in the $a$-spectrum is at energy $\sim 2V_{b}$, as expected for the case of decoupled ladders (see Fig. 2a), but different from the result for larger $t_{a}$.

The numerical data in Fig. 2: for $t_{xy} = 0$ contains already some of the characteristic features of the optical experiments, such as the relative peak positions of the spectra with $a$ and $b$ polarization and also their different spectral weight. Next we consider the role of the hopping $t_{xy}$ along the zig-zag chains of edge sharing VO$_{5}$ pyramids. In Fig. 4 results are shown for $t_{a} = 0.4$, $t_{b} = 0.2$, $t_{xy} = 0.15$ and $V_{a} = V_{b} = 0.8$, $V_{xy} = 0.9$ eV, where the $t_{xy}$ value was optimized to have the best agreement with the experiments given in the inset \[13\]. One important effect of finite $t_{xy}$ is the generation of additional spectral weight on the high energy side of the spectrum. We attribute this to the incoherent motion of excitations along the $a$-direction due to the finite $t_{xy}$. Compared to Fig. 2: the $a$-spectrum shows a prepeak at 0.8 eV and a peak at 1.3 eV due to inter-ladder excitations, which falls in the range of the shoulder in the experimental spectra. There is also a weak low energy absorption below 0.3 eV, reminiscent of the ‘charged magnon’ absorption ob-
The exchange between electrons in different rungs along the transverse field, while the Coulomb interaction between vanadium ions in the rung. The hopping \( t_b \) is small, i.e., less pronounced, which extends up to 2.5 eV. There is no evidence of low energy excitations in \( a \)-polarization the maximum of the absorption is about 0.1-0.15 eV in infrared optics in the range \( \omega \sim 0.01 \) to 0.15 eV. We believe that these are charge excitations, which are activated by spin-charge and inter-ladder coupling, as they disappear in the spinless fermion case or when the hopping between the ladders is switched off (Fig. 3).

For \( b \)-polarization the maximum of the absorption is at 1.15 eV, i.e., slightly higher than the main peak in the \( a \)-spectrum. Again there is high energy spectral weight, although less pronounced, which extends up to 2.5 eV. There is no evidence of low energy excitations in \( \sigma_b(\omega) \), consistent with their absence in experiments.

Temperature effects are small up to 500 K, however there is a decrease of spectral weight in the \( a \)-polarization spectrum for \( \omega < 0.2 \) eV and \( T < 200 \) K. For the chosen parameters, the equal-time density correlation functions indicates a tendency towards a zig-zag pattern, although the charge distribution itself is uniform.

To get a deeper understanding of the optical properties we turn now to a different representation of the low energy degrees of freedom. For large \( U \) and \( V_a \) the relevant subspace of one electron per rung can be represented as eigenstates of spin \( S \) and pseudospin \( T \) operators, where the configurations with \( T_z = \pm \frac{1}{2} \) correspond to the left/right position of the electron within a rung. After projecting out the high energy states we obtain the following Hamiltonian for a single ladder [17]:

\[
H_{\text{ladder}} = -2t_a \sum_r T_r^x + (2V_b + \frac{2t_b^2}{\Delta}) \sum_r T_r^z T_{r+b}^z
+ \frac{4t_b^2}{\Delta} \sum_r (S_r \cdot S_{r+b} - \frac{1}{4})(T_r^+ T_{r+b}^- + \text{H.c.})
\] (4)

where \( r \) indicates a composite site formed by the two vanadium ions in the rung. The hopping \( t_a \) acts like a transverse field, while the Coulomb interaction between electrons on neighbor rungs \( r \) and \( r+b \) in the ladder is like the \( zz \) term in the Ising model. The third term is due to the exchange between electrons in different rungs along the \( b \) direction. The value of \( \Delta \) scales between \( V_a + V_b \) and \( 2t_a \) depending on which scale of energy is larger.

The coupling between neighboring ladders yields

\[
H_{\text{inter-ladder}} = -V_{xy} \sum_{(r_1, r_2)} (T_{r_1}^z - \frac{1}{2})(T_{r_2}^z + \frac{1}{2})
+ \frac{4t_{xy}^2}{\Delta_1} \sum_{(r_1, r_2)} (S_{r_1} \cdot S_{r_2} - \frac{1}{4})(T_{r_1}^z T_{r_2}^- + \frac{1}{4})
\] (5)

with \( r_2 = r_1 + (\frac{a}{2}, \pm \frac{b}{2}) \) and \( \Delta_1 = 2V_b + V_a - V_{xy} \). In this representation \( \sigma_a(\omega) \) is given by the transverse response function \( \langle T_{-q}^y T_{q}^y \rangle \) with \( q = (0, 0) \) if \( t_{xy} = 0 \). The latter is shown in the insets of Fig. 3 and has been evaluated by means of the FTLM using the same parameters as for the \( t-J-V \) model and assuming that the spin correlations can be treated as for valence-bond states, i.e., \( \langle S_{r_1} \cdot S_{r_2} \rangle = -\frac{3}{4} \). As one can see the main peak position and its \( V_{xy} \) dependence are properly described. The dominant pole structure is consistent with the excitonic nature of the optical absorption. The spectral broadening in the complete \( t-J-V \) model can be attributed to the dynamical character of the spin degrees of freedom.

The strong \( V_{xy} \) dependence of the peak position in the \( a \)-spectrum cannot be understood if \( 2t_a/V_b \) is small, i.e., when the ground state has a simple zig-zag charge order pattern, corresponding to a classical Néel order of pseudospins. In this case due to the geometry of the inter-ladder bonds the flipping of a pseudospin, i.e., moving an electron from left (right) to right (left), does not change the number of frustrated bonds with energy \( \sim V_{xy} \), and the excitation energy is \( 2V_b \). This case is sketched in Fig. 3, which shows a single flipped spin in an otherwise Néel ordered neighborhood. By flipping a further pseudospin in the neighboring ladder, however, e.g. by
FIG. 5. Configuration with one (a) and two pairs of domain-walls (b). The pseudospin pointing to the left (right) direction indicate a charge configuration with the electron on the left (right) position in the rung, respectively. Black (gray) stripes show the bond where electrons of neighboring rungs which belong to different ladders feel the Coulomb repulsion $V_{xy}$ before (after) flipping one (a) and two (b) pseudospins.

an optical excitation, one can reach the configuration of Fig. 3 with one frustrated bond less compared to the starting configuration (Fig. 5), which leads to a reduction of the excitation energy $V_{xy}$. Such processes can be neglected in the $2t_a/V_b \rightarrow 0$ limit. However, when the system is close to its critical point, i.e., $2t_a/V_b \sim 1$, the ground state is dominated by configurations with a high density of domain walls. In this case most optical excitation processes occur in the neighborhood of already existing domain walls. This implies that near criticality even though the energy of the ground state is not strongly affected by $V_{xy}$, the excitation spectrum undergoes significant changes. The excitation energy is lowered by the repulsion $V_{xy}$ as shown in Fig. 5.

Finally, we address the low-energy features appearing in the $a$-spectra by considering the single chain Ising model in a transverse field, i.e., given by the terms $\propto t_a$ and $V_a$ in Eq. (4). The excitation spectrum of this model is described by the domain wall dispersion of the form $\omega = V_b \sqrt{1 + h^2 + 2h \cos(q)}$, with $h = 2t_a/V_b \pi$. There are low-energy charge excitations near $q = \pi$ connected to the slow dynamics of the domain walls close to the critical point, which can however not be optically excited. The optical response for $a$-polarization is determined by the excitation of $q \sim 0$ pairs of domain walls whose energy only slightly deviates from the static charge gap value $2V_b$. Yet this supports the idea that the low-energy excitations in Fig. 4 can be attributed to these low-energy charge excitations, namely optically activated by spin scattering and by the interladder coupling. This can be corroborated by a simplified version of Hamiltonian (4) where the spins are assumed to be disordered and static, i.e., by introducing random variables for $(S^-_n S^-_{n+h})$. In contrast to the ‘charged magnon’ scenario [4], the energy scale is determined here by the domain wall motion.

We conclude that the optical response at room-temperature can be well described by the quarter-filled $t$-$J$-$V$ model, assuming that the system is close to criticality $2t_a \sim V_b$. Hence, strong valence fluctuations connected to domain wall dynamics, which have not been considered in previous studies, play a crucial role for the understanding of the charge ordering transition and the charge pattern of the ground state in the low temperature phase. The comparison with the experimental data also indicates the importance of both the inter-ladder hopping $t_{xy}$ and the Coulomb repulsion $V_{xy}$. Finally, we note that the nature of the single particle excitations for the present model is a completely open issue. Spectral distributions obtained recently by ARPES measurements are highly anomalous [26], but have been interpreted by the charge-spin separation of a doped Heisenberg chain. It is natural to expect that the domain wall excitations significantly influence the character of the single particle electron Green’s function.

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