Charge excitations in LiV$_2$O$_5$ and NaV$_2$O$_5$: similarities and differences

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We calculate the optical conductivity of LiV$_2$O$_5$ and NaV$_2$O$_5$ using exact numerical diagonalization of a quarter-filled extended Hubbard model on a system of coupled ladders. In particular, electronic correlations are treated exactly, and a quantitative agreement between calculated and experimentally observed optical conductivity of these two vanadium oxides is presented. Furthermore, it is found that LiV$_2$O$_5$ differs from NaV$_2$O$_5$ not only in the charge ordering pattern but also in the nature of the inter-ladder coupling: In contrast to LiV$_2$O$_5$, in NaV$_2$O$_5$, neighboring ladders are coupled by a strong Coulomb repulsion, and not by inter-ladder hopping.

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In the past years, low-dimensional transition metal compounds have been intensively investigated because of their unconventional spin and charge excitation spectra. In this respect, the vanadate $\alpha'$-NaV$_2$O$_5$ has attracted particular interest as a ladder system at quarter filling, containing only one equivalent V site with a formal valence $+4$. The magnetic susceptibility of NaV$_2$O$_5$ can be well described by a $S = 1/2$ antiferromagnetic Heisenberg chain with exchange interactions of $J = 440$ and 560 K for temperatures below and above the transition temperature $T_C \approx 34$ K. The low-temperature phase is found to be charge ordered, but the nature of this transition is still under discussion. The much less studied $\gamma$-LiV$_2$O$_5$ belongs to the same family of vanadium oxides and exhibits a one-dimensional $S = 1/2$ Heisenberg like behavior with an exchange interaction of $J = 308$ K. In contrast to NaV$_2$O$_5$, there is no indication of a phase transition at lower temperature. Since both compounds are structurally related it is interesting to clarify the microscopic origin of the different physical properties of both vanadates. This will be discussed in this paper on the basis of the optical conductivity.

Recently, the optical conductivity of LiV$_2$O$_5$ and NaV$_2$O$_5$ has been measured. In the energy range from 0 to 3 eV similar peaks in the $E \parallel a$ spectra of both materials were found. On the other hand, a complete suppression of the peaks in the $E \parallel b$ spectrum of LiV$_2$O$_5$ was observed. In this paper, we show that this suppression results not only from the double chain charge ordering pattern but also from the strong inter-ladder hopping in LiV$_2$O$_5$. Consequently, it is found that both vanadates differ not only in the charge ordering pattern but also in the nature of the inter-ladder coupling. Recently, we studied the optical conductivity of NaV$_2$O$_5$ so that in the present paper we concentrate on LiV$_2$O$_5$ and on the comparison of both vanadium oxides.

At room temperature LiV$_2$O$_5$ and NaV$_2$O$_5$ have orthorhombic crystal structures that are described by space groups $Pnma$ and $Pmmn$, respectively. Both compounds consist of layers of VO$_5$ square pyramids (see Fig. 1). In contrast to NaV$_2$O$_5$, a structural analysis for LiV$_2$O$_5$ shows two inequivalent vanadium sites which were also found by NMR experiments. These two vanadium sites were assigned a valence of V$^{4+}$ and V$^{5+}$, respectively, and they form two different zig-zag chains along the $b$ direction. Therefore, magnetic V$^{4+}$ double chains are separated by nonmagnetic V$^{5+}$ double chains. Note that this charge ordering pattern is not comparable with the in-line order discussed for NaV$_2$O$_5$. As can be seen from Fig. 1, the VO layers are more corrugated in LiV$_2$O$_5$ than in NaV$_2$O$_5$ because the Li atoms are smaller than the Na atoms.

FIG. 1. Representation of the (a) NaV$_2$O$_5$ and (b) LiV$_2$O$_5$ room temperature crystal structure. (c) shows a schematic projection of the LiV$_2$O$_5$ structure onto a $(a,b)$ plane where only the vanadium ions are drawn.

In Ref. we studied the optical conductivity of NaV$_2$O$_5$ using a quarter-filled extended Hubbard model of the V 3$d$ electrons on the vanadium lattice which forms...
a coupled ladder system. In the present study we modify this model for LiV$_2$O$_5$ by an additional on-site energy $\varepsilon_i$

$$\mathcal{H} = - \sum_{\langle i,j \rangle, \sigma} t_{ij} \left( c_{i,\sigma}^\dagger c_{j,\sigma} + \text{H.c.} \right) + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

$$+ \sum_i V_{i,j} n_i n_j + \sum_i \varepsilon_i n_i$$  \hspace{1cm} (1) 

to cause the double chain charge ordering observed in LiV$_2$O$_5$ [14]. In Eq. (1) $\langle i,j \rangle$ denotes summation over all pairs of nearest neighbors, and spin $\sigma = \uparrow, \downarrow$. $c_{i,\sigma}^\dagger$, $c_{i,\sigma}$ are electron creation operators at vanadium sites, $n_i = \sum_\sigma c_{i,\sigma}^\dagger c_{i,\sigma}$ is the occupation-number operator, and $U$ denotes the Coulomb repulsion between electrons on the same site. The hopping parameters $t_{ij}$ of Eq. (1) are defined in panel (c) of Fig. 1. The inter-site Coulomb interactions $V_{i,j}$ between nearest vanadium neighbors on a rung, on a leg or on different ladders are $V_a$, $V_b$ and $V_{xy}$. The on-site energy $\varepsilon_i$ is $-\Delta/2$ ($\Delta/2$) for the V$^{4+}$ ($V^{5+}$) sites [see panel (c) in Fig. 1]. In contrast to NaV$_2$O$_5$, in LiV$_2$O$_5$ the ladders are less strictly situated in an (a,b) plane (see Fig. 1). Thus, the system shown in panel (c) of Fig. 1 has more 3D character than NaV$_2$O$_5$.

For an insulating system, the optical conductivity $\sigma_{\alpha}(\omega)$ is given by the Kubo formula for finite frequency response

$$\sigma_{\alpha}(\omega) = \frac{1}{\omega} \text{Re} \int_0^\infty dt e^{i\omega t} \langle 0 | j_{\alpha}(t) j_{\alpha} | 0 \rangle. \hspace{1cm} (2)$$

Here $j_{\alpha}$ with $\alpha = a, b$ are the components of the current operator parallel to $a$ or $b$ direction. Equation (2) is valid for zero temperature, whereas the experiments have been carried out at finite temperatures [17]. However, it is known from both experiment and theory that at least the spectra for NaV$_2$O$_5$ depend only weakly on temperature [18,19]. Therefore, we may restrict ourselves to calculations for zero temperature.

In the following we evaluate Eq. (2) using the standard Lanczos algorithm [20] which is limited to small clusters. Therefore, first we have to check if our results are sufficiently converged with respect to system size. Since the hopping between $V^{5+}$ ions in LiV$_2$O$_5$ is very small [21], this material can be described by the double ladder system shown in panel (c) of Fig. 1. Consequently, the system is infinite only in $b$-direction, and we shall always use open boundary conditions for this direction (to enlarge the effective cluster size). However, one has to make sure that electrons on the edges of the cluster are still embedded in the local Coulomb potential that results from the double chain charge ordering. For this purpose, sites on the edges of the clusters that are occupied in the perfectly ordered state need an additional on-site energy $V_0$ to simulate the influence of occupied sites outside of the cluster. To prove that the results are sufficiently converged with respect to system size we have evaluated the double ladder system shown in panel (c) of Fig. 1 both with open and periodic boundary conditions and found only small differences (not shown).

The distances within the vanadium ladder structures in LiV$_2$O$_5$ and NaV$_2$O$_5$ are similar. Therefore, we start from the parameters of the ladder used in Ref. [14] for NaV$_2$O$_5$ ($t_a = 0.38$ eV, $t_b = 0.17$ eV, $t_{\text{diag}} = 0$, $V_a = 0.8$ eV, $V_b = 0.6$ eV, $U = 2.8$ eV) to describe the optical conductivity of LiV$_2$O$_5$. Consequently, we have to determine only three parameter values, $\Delta$, $V_{xy}$, and $t_{xy}$. For LiV$_2$O$_5$ the choice $V_{xy} = 0$ is possible because the Coulomb repulsion between nearest neighbors of neighboring ladders counteracts the double chain charge ordering caused by $\Delta$. This means that the parameters $\Delta$ and $V_{xy}$ are not independent from each other.

![FIG. 2. Optical conductivity [panel (a): $\sigma_a(\omega)$, panel (b): $\sigma_b(\omega)$] of a single ladder ($t_{xy} = 0$) where the hopping parameters from Ref. 14 (dotted lines, $t_a = 0.38$ eV, $t_b = 0.17$ eV, $t_{\text{diag}} = 0$) and from Ref. 21 (dashed lines, $t_a = 0.35$ eV, $t_b = 0.02$ eV, $t_{\text{diag}} = 0.1$ eV) were used. In addition, the results for the double ladder system shown in panel (c) of Fig. 1 ($t_a = 0.35$ eV, $t_b = 0.02$ eV, $t_{\text{diag}} = 0.1$ eV, $t_{xy} = -0.18$ eV) is plotted with full lines. The parameters of the Coulomb interaction are $U = 2.8$ eV, $V_a = 0.8$ eV, $V_b = 0.6$ eV, $V_{xy} = 0$, and $\Delta = 1.7$ eV. The theoretical line spectra are broadened with Gaussian function of width 0.1 eV.]

First we discuss the case of a single ladder ($t_{xy} = 0$) for which the optical conductivity is shown as dotted lines in Fig. 1. As can be seen from panel (a) of Fig. 2, $\sigma_a$ is dominated by an excitation at 1.0 eV which corresponds to a transition from a bonding to an anti-bonding state of a singly occupied rung that has been discussed before for NaV$_2$O$_5$ [22]. If one considers a single rung one obtains $\sqrt{\delta^2 + 4t_b^2}$ for the excitation energy of this transition where an effective on-site energy $\delta = \Delta - 2V_b$ has to be used to take the chain charge ordering into account. Therefore, the on-site energy $\Delta$ determines the
excitation energy (of the transition from a bonding to an anti-bonding state). A value of $\Delta = 1.7$ eV can be obtained directly from the experimentally observed peak position \[\text{[2]}\]. In contrast to $\sigma_a$, for $\sigma_b$ we find two basic mechanisms for excitations. The structures at 1.2 eV and 1.8 eV [see dotted line in panel (b) of Fig. 3] can be interpreted as a transition to states with one unoccupied and one doubly occupied rung [excitation energies $\sim (\Delta + V_a - 2V_b)$ and $\sim (\Delta + V_a - V_b)$]. The excitations around 2.8 eV result from the creation of one doubly occupied site (excitation energy $\sim U$).

Next we discuss the influence of the inter-ladder hopping $t_{xy}$ on the optical conductivity. A moderate value of $t_{xy}$ affects $\sigma_a$ only weakly and leads, on the other hand, to a suppression of low-energy peaks in $\sigma_b$ (not shown). This suppression becomes stronger if $\Delta$ increases. (Because of different charge ordering pattern this influence of $\Delta$ is not identical with the findings in Ref. [23].) One would obtain good agreement between the calculated and the experimentally observed [2] optical conductivity for $t_{xy} = 0.3 \ldots 0.4$ eV. However, according to Ref. [2], the magnetic properties of the model along $b$-direction can be described by a single Heisenberg chain along a zig-zag line. The choice of $t_{xy} = 0.3 \ldots 0.4$ eV for the inter-ladder hopping supposed above would lead to a strong frustration [24]

$$J_b / J_{xy} = \frac{t_b^2}{(U - V_b)} \approx 0.3$$

which is not in accordance with NMR [1] and susceptibility measurements [10]. However, this discrepancy is caused by neglecting the diagonal hopping $t_{\text{diag}}$: Tight-binding fits to the band structure found in LDA calculations with nonzero $t_{\text{diag}}$ lead to a small value of $t_b$ both for NaV$_2$O$_5$ and for LiV$_2$O$_5$ [23,21]. Therefore, we use in the following the set of tight-binding parameters from Ref. [21] for LiV$_2$O$_5$ ($t_a = 0.35$ eV, $t_b = 0.02$ eV, $t_{\text{diag}} = 0.1$ eV, $t_{xy} = -0.18$ eV). Since the diagonal hopping $t_{\text{diag}}$ is included, the frustration parameter [2] is now negligibly small [2]. The Coulomb interactions $U$, $V_a$, and $V_b$ of the ladder are not changed. In contrast to LiV$_2$O$_5$, for NaV$_2$O$_5$ we use a parameter set with $t_{\text{diag}} = 0$ as in Ref. [13] to avoid strong finite-size effects [20].

From a comparison of the optical conductivity of a single ladder for both parameter sets (dotted and dashed lines in Fig. 3) one can conclude that the results are not fundamentally changed by the tight-binding parameters from Ref. [21]. But these new parameters lead to a significantly decreased spectral weight of the low-energy structure in $\sigma_b$ because the mobility of a created doubly occupied rung is now more restricted due to the small value of $t_b$. Nevertheless, the above analysis of the basic mechanisms for excitations on a single ladder remains valid even for $t_{\text{diag}} \neq 0$.

Now we return to the influence of the inter-ladder hopping on the optical conductivity. For this purpose, we compare in Fig. 2 the results of a single ladder (dashed lines) with the optical conductivity for the complete double ladder system shown in panel (c) of Fig. 1 (full lines) where we use the hopping parameters from Ref. [21]. As can be seen from panel (a) the excitation resulting from the transition between a bonding and an anti-bonding state of a rung discussed above depends only weakly on $t_{xy}$. In contrast to $\sigma_a$, $\sigma_b$ is changed strongly by a finite $t_{xy}$. In particular, some new structures arise, and the spectral weight is divided among different excitations. Note that the influence of $t_{xy}$ does not depend on its sign.

In Fig. 3 the calculated optical conductivities for LiV$_2$O$_5$ and NaV$_2$O$_5$ [panels (a) and (c)] are compared to the experimental spectra [panels (b) and (d)] from Ref. [2]. We restrict the following discussion of the optical conductivity to the energy range up to 2 eV since transitions with a higher excitation energy involve oxygen orbitals [2]. Good agreement for the optical conductivity of NaV$_2$O$_5$ is found [compare panels (c) and (d) of Fig. 3] where the hopping parameters ($t_a = 0.38$ eV, $t_b = 0.17$ eV, $t_{xy} = 0.012$ eV) and the on-site Hubbard interaction ($U = 2.8$ eV) are taken from Ref. [3]. The values of the intersite Coulomb interactions $V_a = 0.8$ eV, $V_b = 0.6$ eV and $V_{xy} = 0.9$ eV have been adjusted to obtain correct peak positions (for details see Ref. [3]):
Note that the loss function in EELS experiments for NaV$_2$O$_5$ can also be described with the same Hamiltonian, and the same set of model parameters [13]. For LiV$_2$O$_5$, we obtain good agreement of the calculated optical conductivity [panel (a) of Fig. 3] and the experimental data of Ref. [12] [panel (b) of Fig. 3]. Again we use the hopping parameters from LDA calculations [21] ($t_a = 0.35$ eV, $t_b = 0.02$ eV, $t_{\text{diag}} = 0.1$ eV, $t_{xy} = -0.18$ eV) and the Coulomb interactions of the ladder ($U = 2.8$ eV, $V_a = 0.8$ eV, $V_b = 0.6$ eV) found for NaV$_2$O$_5$. The on-site energy $\Delta = 1.7$ eV is adjusted to obtain the correct peak position of $\sigma_0$. Thus we use only one free parameter for LiV$_2$O$_5$. The effective on-site energy $\delta = \Delta - 2V_b = 0.5$ eV that determines the charge ordering along the chains agrees well with the value $\delta = 0.3$ eV found in Ref. [21]. To summarize the comparison of the calculated and the experimentally observed optical conductivity for LiV$_2$O$_5$ and NaV$_2$O$_5$ (Fig. 3) one can state that a good agreement is found for both vanadates. In particular, the complete suppression of the low energy structure in $\sigma_0$ of LiV$_2$O$_5$, and the peak shapes are reproduced.

Finally, we want to compare the results for LiV$_2$O$_5$ and NaV$_2$O$_5$ in some detail. As shown above, the ladder parameters are similar for both compounds. This means that the electronic properties of the single ladders are similar in LiV$_2$O$_5$ and NaV$_2$O$_5$ even though one finds a double chain charge ordering in LiV$_2$O$_5$ caused by an on-site energy $\Delta$. Apart from that, the main difference between LiV$_2$O$_5$ and NaV$_2$O$_5$ is the character of the inter-ladder coupling. In LiV$_2$O$_5$ one finds a strong inter-ladder hopping $t_{xy}$ [keep in mind that this coupling does not go beyond the double ladder systems shown in panel (c) of Fig. 1] which is very small in NaV$_2$O$_5$. On the other hand, in NaV$_2$O$_5$ the ladders are coupled due to a strong inter-ladder Coulomb interaction $V_{xy}$. Note again that the choice $V_{xy} = 0$ is reasonable for LiV$_2$O$_5$ since $\Delta$ and $V_{xy}$ are not independent from each other. The character of the inter-ladder coupling determines the low energy features of $\sigma_0$: the well defined structure in NaV$_2$O$_5$ is suppressed in LiV$_2$O$_5$ (see Fig. 3) where a finite $t_{xy}$ leads to new excitations among which the spectral weight is divided.

In conclusion, we have obtained a quantitative description of the highly anisotropic optical conductivity of LiV$_2$O$_5$ and NaV$_2$O$_5$ by exact diagonalization of small clusters. In particular, the complete suppression of the low-energy peaks in the spectrum of LiV$_2$O$_5$ with electrical field parallel to the leg direction is reproduced. The good agreement of calculated and experimental optical conductivity for both vanadates implies that the electronic properties of the single ladders are similar in LiV$_2$O$_5$ and NaV$_2$O$_5$ (even though one finds a double chain charge ordering in LiV$_2$O$_5$). The main differences between the optical properties of LiV$_2$O$_5$ and NaV$_2$O$_5$ are due to the completely different nature of the inter-ladder coupling. In contrast to LiV$_2$O$_5$, in NaV$_2$O$_5$ different ladders are coupled by a strong Coulomb repulsion $V_{xy}$ and not by inter-ladder hopping $t_{xy}$. Because of the on-site energy $\Delta$ LiV$_2$O$_5$ can be viewed as an asymmetric quarter-filled ladder compound. Therefore, it would be interesting to compare with other experiments probing charge excitations like EELS or XPS.

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