Optical Conductivity of the Trellis-Lattice $t$-$J$ Model:
Charge Fluctuations in NaV$_2$O$_5$

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Optical conductivity of the trellis lattice $t$-$J$ model at quarter filling is calculated by an exact-diagonalization technique on small clusters, whereby the valence state of V ions of NaV$_2$O$_5$ is considered. We show that the experimental features at $\sim$1 eV, including peak positions, presence of shoulders, and anisotropic spectral weight, can be reproduced in reasonable range of parameter values, only by assuming that the system is in the charge disproportionated ground state. Possible reconciliation with experimental data suggesting the presence of uniform ladders at $T > T_c$ is discussed.

KEYWORDS: NaV$_2$O$_5$, optical conductivity, $t$-$J$ ladder, charge fluctuation, trellis lattice, spin-Peierls

The valence state of V ions in NaV$_2$O$_5$, a compound once believed to be a typical spin-Peierls system, has become an issue of intense controversy even above the transition temperature $T_c$; recent X-ray structural analysis and other experiments[1-7] seem to suggest the uniform valence of V$^{4.5+}$, the system being the coupled uniform ladders at quarter filling, whereas an interpretation of low-energy optical conductivity data suggests the system to be in a broken-parity electronic ground state. To clarify this issue will help one understand the mechanism of the phase transition of this compound observed at $T_c = 34$ K.

In this letter, we consider this issue by calculating the optical conductivity $\sigma(\omega)$ of the trellis-lattice $t$-$J$ model at quarter filling directly. We will show that the experimental features of $\sigma(\omega)$ at $\omega \simeq 0.6 - 2.5$ eV, such as the positions of the main peak and its shoulders, anisotropy in the spectral weight, etc., observed over a wide temperature range above and below $T_c$, can be explained within a reasonable range of parameter values, only by assuming that the system is in the charge disproportionated ground state. We will thereby point out that the difference in the time scale of the measurements may be a possible way of reconciliation: charge (or valence) fluctuation of V ions is slow compared with the frequency of electric field of light used in the optical measurement, but it is fast enough compared with the time scale of the other measurements. We would suggest that measurements of frequency range of $\sim$50 GHz to $\sim$1 THz should be able to detect a possible resonant charge fluctuation in this compound.

The low-energy electronic state of the two-dimensional plane of NaV$_2$O$_5$ may be written by the trellis-lattice $t$-$J$ model, i.e., coupled anisotropic $t$-$J$ ladders (see Fig. 1), as we have shown in ref. 1. The Hamiltonian is given by

$$H = - \sum_{\langle ij \rangle \sigma} t_{ij} (\hat{c}_{i\sigma}^{\dagger} \hat{c}_{j\sigma} + \text{H.c.})$$

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. It also represents the zigzag chain bonds with parameters $t_{xy}$ and $J_{xy}$ where the intersite Coulomb repulsion $V_{xy}$ is also taken into account. We introduce the ‘symmetry-breaking’ on-site energy of an electron, $\Delta_i$, which takes either $\Delta \geq 0$ or 0 depending on sites, whereby we can make the system charge disproportionated if $\Delta \neq 0$. $c_{i\sigma}^{\dagger} = c_{i\sigma}^{\dagger} (1 - n_{i-\sigma})$ is the constrained electron-creation operator at site $i$ and spin $\sigma (=\uparrow, \downarrow)$, $S_i$ is the spin-$\frac{1}{2}$ operator, and $n_i = n_{i\uparrow} + n_{i\downarrow}$

$$+ \sum_{\langle ij \rangle} J_{ij} (S_i \cdot S_j - \frac{1}{4} n_i n_j)$$
$$+ \sum_{i} V_{i} n_i n_j + \sum_{i} \Delta_i n_i,
$$ (0.1)
is the electron-number operator. We consider the case at quarter filling.

We employ a Lanczos exact-diagonalization technique on small clusters and calculate the frequency-dependent conductivity $\sigma(\omega)$ to examine the anisotropic optical response of the system. A finite-size cluster of the trellis lattice, i.e., coupled two $4 \times 2$ ladders shown in Fig. 1, is used with periodic boundary condition. The optical conductivity is defined by

$$\sigma_\alpha(\omega) = \sum_{\nu \neq 0} \frac{1}{\omega} |\langle \psi_\nu | j_\alpha | \psi_0 \rangle|^2 \delta(\omega - (E_\nu - E_0)),$$

where $|\psi_\nu\rangle$ denotes the $\nu$-th eigenstate (eigenenergy) of the system (in particular, $\nu = 0$ denotes the ground state). Also, $j_\alpha$ with $\alpha = a, b$ denotes a component of the current operator

$$j_\alpha = i \sum_{ij} t_{ij}(r_i - r_j)_{\alpha} \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma},$$

where $(r_i - r_j)_{\alpha}$ is the $\alpha$-component of the vector connecting between sites $i$ and $j$. The system we treat is in the insulating state and there is no Drude peak at $\omega = 0$.

We use the following two sets of values of the ladder parameters (in units of eV) obtained from the $d$-$p$ model by the method of ref. [11]. Set A: $t_\perp = 0.298$, $t_0 = 0.140$, $J_{\parallel} = 0.0487$, and $J_b = 0.0293$, which are obtained in ref. [11] using realistic values of the $d$-$p$ model parameters $t_{pd} = 1.22$ (1.03) for the hopping integral of the rung (leg) V-O bonds, $U_d = 4.0$ for the on-site Coulomb repulsion on V ions, and $\Delta_{pd} = 4.0$ (6.5) for the energy-level difference between the V $d_{xy}$-orbital and O $p$-orbital on the rung (leg). Set B: $t_\perp = 0.397$, $t_0 = 0.194$, $J_{\parallel} = 0.0658$, and $J_b = 0.0546$, which are obtained using a different set of values of the $d$-$p$ model parameters with enhanced hopping amplitude: $t_{pd} = 1.46$ (1.24), $U_d = 5.0$, and $\Delta_{pd} = 4.0$ (6.5) for the rung (leg) V-O bonds. Values of the other parameters $t_{xy}$, $V_{xy}$, and $\Delta$ are then varied for simulating various situations. We use the relation $J_{xy} = 4t_{xy}^2/U_d$ for simplicity.

The optical conductivity observed in experiment has the following features: (i) Onset of charge-transfer excitations from O $p_{x,y}$- or $p_y$- to V $d_{xy}$-orbitals appears at $\omega \simeq 3 - 3.5$ eV which is anisotropic between $a \parallel E$ and $b \parallel E$. (ii) There appear broad spectral features around $\omega \simeq 1$ eV, which have been identified as the $d$-$d$ transitions, and the main peak has a shoulder in $\sim 0.5$ eV ($\sim 0.8$ eV) higher-energy side in $\sigma_a(\omega)$ ($\sigma_b(\omega)$). Also the height of the peaks (or the integrated spectral weight) is markedly larger in $a \parallel E$ than in $b \parallel E$. (iii) There is a small continuum in the low-energy region of $\omega \simeq 0.01 - 0.1$ eV, the origin of which was argued to be ‘charged magnons’. The spectral features (i) and (ii) are hardly changed over a wide temperature range above and below $T_c$, while the oscillator strength of the feature (iii) decreases suddenly at $T_c$ with lowering temperatures. We now want to discuss the origins of the features (ii).

Let us first take some simplified pictures. Suppose an isolated rung of the ladder, then we have the $d$-$d$ excitation peak in $\sigma_a(\omega)$ at $\omega = \sqrt{(2t_\perp)^2 + \Delta^2}$, the value of which is however too small compared to $\omega \simeq 1$ eV if $\Delta = 0$ or there is no charge disproportionation, because the effective hopping amplitude $t_\perp \simeq 0.3$ eV strongly reduced from the bare $d$-$p$ hybridization $t_{pd}$ relevant here. Suppose next the trellis lattice in the limit of small hopping amplitude and large $V_{xy}$ and/or $\Delta$ where the sites of, say, the right legs of the ladders are all with $\Delta > 0$ and those of the left with $\Delta = 0$ (resulting in the charge disproportionated ground state), then we have a peak in $\sigma_a(\omega)$ at $\omega = \Delta + 2V_{xy}$. This is because the electron transferred through the rung interacts (by $V_{xy}$) with two electrons on the leg of the neighboring ladder across the zigzag chain bonds; the peak position can be comparable to $\omega \simeq 1$ eV because $V_{xy} \simeq 0.5$ eV is enough even at $\Delta = 0$. If small randomness occurs in the disproportionated charge configuration, then another peak can also appear at $\omega = \Delta + V_{xy}$, because the transferred electron may interact with only one electron on the leg of the neighboring ladder across the zigzag chain bonds. Thus, there appears a two-peak structure in $\sigma_a(\omega)$ (which, as we will see below, corresponds to

Fig. 2. Optical conductivity $\sigma_a(\omega)$ calculated for the trellis-lattice $t-J$ model with $\Delta = 0$. Solid and dashed curves show $\sigma_a(\omega)$ for $a \parallel E$ and $\sigma_b(\omega)$ for $b \parallel E$, respectively. In (a) and (c), we use values of the ladder parameters of Set A, and in (b), we use those of Set B. All the $\delta$-functions in Eq. (2) are Lorentzian broadened with the width of $0.05$ eV. Peaks at $\omega = 0$, which appear due to the broadening and factor $1/\omega$ in Eq. (2), are spurious.
the experimental broad features around $\omega \simeq 1$ eV). It is also noted that, if the charge configuration completely disproportionated on one side of the legs is assumed, the spectral weight for $b \parallel E$ becomes quite small, because the electrons are hard to oscillate along the $b$-direction due to the strong on-site Coulomb repulsion (or prohibited double occupancy in our model) and small values of $t_{xy}$; any randomness in this charge configuration would however make the spectral weight $\sigma_b(\omega)$ larger.

Now let us see the calculated results for $\sigma_a(\omega)$ with keeping these ideas in mind. We first of all find in Fig. 2(a), where we use the parameter Set A with $\Delta = 0$ and $V_{xy} = 0$ (i.e., without charge disproportionation), that the main features appeared at $\omega \simeq 0.5$ eV are again too low in energy compared with experiment. The parameter Set B with $\Delta = 0$ and $V_{xy} = 0$ also gives similar results. We also find that the relative main-peak positions between $a \parallel E$ and $b \parallel E$ are sensitive to the changes in small parameter values $t_{xy}$ and $V_{xy}$ and that some broadened features in $\sigma_a(\omega)$ are induced by the presence of $t_{xy}$. We however find that the essential spectral features, i.e., the overall main-peak positions, remain unchanged. These results thus demonstrate that the $\omega \simeq 1$ eV features cannot be reproduced in reasonable parameter range, without charge disproportionation.

The charge disproportionated ground state can be achieved by including either the large intersite Coulomb repulsion $V_{xy}$ along the zigzag chain bonds or the on-site energy-level difference $\Delta$ between, say, the left and right legs of the ladders. In the former case, the calculated charge correlation functions $\langle n_i n_j \rangle$ indicate that at $V_{xy} \gtrsim 0.6 - 0.7$ eV the strong tendency toward charge disproportionation comes out, although the symmetry is not really broken in finite-size systems. Figures 2(b) and (c) show the results for such situations. Here we assume $V_{xy} = 1.0$ eV, and use values of the parameter Set B with $t_{xy} = 0.1$ eV and Set A with $t_{xy} = 0.05$ eV in Figs. 2(b) and (c), respectively. We find in both figures that the broad spectral features in $\sigma_a(\omega)$ around $\omega \simeq 1$ eV really appear and some smaller features also appear at $\omega \simeq 2$ eV. We analyze the final states corresponding to the largest peaks and find that the features at $\sim 1$ eV come mainly from the states with $\omega \simeq V_{xy}$, and the features at $\sim 2$ eV come mainly from the states with $\omega \simeq 2V_{xy}$, as we have discussed above using simplified pictures. The anisotropy in $\sigma_a(\omega)$ between $a \parallel E$ and $b \parallel E$ is also noted; the main peak in $\sigma_b(\omega)$ is located in $\sim 0.5$ eV higher energy side than that in $\sigma_a(\omega)$ and the spectral weight for $\sigma_b(\omega)$ is considerably smaller than that for $\sigma_a(\omega)$. These results are all in good agreement with experiment. To get more precise agreement with experimental features would necessitates the calculations in larger size clusters, which are however not feasible in cluster diagonalizations.

Next let us see the results obtained by introducing $\Delta \neq 0$ to break the symmetry and actually realizing the charge-disproportionated ground state. Note that although such an ad hoc assumption of the presence of nonzero $\Delta$ induces charge disproportionation in the system, its origin or the mechanism of appearing $\Delta \neq 0$ should be clarified; the simplest explanation may be the presence of strong intersite Coulomb repulsions, which induces the broken-symmetry ground state in the thermodynamic limit and leads to $\Delta \neq 0$. The calculated results for $\sigma_a(\omega)$ are shown in Fig. 3 where we assume that the sites of the right legs of the ladders are all with $\Delta > 0$ and those of the left are all with $\Delta = 0$. The ladder parameters of Set A are used. We assume $\Delta = 0.3$, $V_{xy} = 0.2$, and $t_{xy} = 0.03$ eV in Fig. 3(a), which result in the valences of $V^{4.789+}$ and $V^{4.211+}$; here we find that the peak positions in $\sigma_a(\omega)$ are again still too low compared with experiment. By increasing the values of $\Delta$ and $V_{xy}$, we find that the peak positions shift to higher energy side and the agreement with experiment becomes better; in Fig. 3(b), we assume $\Delta = 0.4$, $V_{xy} = 0.5$, and $t_{xy} = 0.05$ eV, which result in the valences of $V^{4.940+}$ and $V^{4.060+}$, and in Fig. 3(c), we assume $\Delta = 0.4$, $V_{xy} = 0.5$, and $t_{xy} = 0.03$ eV, which result in the valences of $V^{4.943+}$ and $V^{4.057+}$. In the latter two cases, we find that (i) the main peak appears at $\omega \simeq 1$ eV and its shoulders at $\omega \simeq 1.6$ eV in both $\sigma_a(\omega)$ and $\sigma_b(\omega)$ where the distance between the main peaks and shoulders is controlled primarily by the value of $V_{xy}$, (ii) the main-peak position in $\sigma_b(\omega)$ is slightly higher in energy than that in $\sigma_a(\omega)$, and (iii) the strong anisotropy of the spectral weight between $a \parallel E$ and $b \parallel E$ appears. These results are all in good quali-
tative agreement with experiment. We furthermore find that the broad main peak has some internal structures, which may correspond to the experimentally observed broad peak which also has some structures.

We note that the anisotropy in the spectral weight between $a \parallel E$ and $b \parallel E$ which is seen in Figs. 3(b) and (c) is too strong compared with the experimental anisotropy. This might suggest that the charge-ordering pattern assumed above should be made more ‘random’, so that the electrons may oscillate along the legs of the ladders. To check this idea and to improve the strength of the anisotropy, we also used the charge-ordering pattern called the zigzag structure [12, 13] which was argued to be realistic at $T < T_c$. The calculated result for $\sigma_\parallel(\omega)$ is shown in Fig. 4, where we indeed find that the spectral weight of $\sigma_\parallel(\omega)$ is much increased without changing other features, resulting in a very good agreement with the experimental features.

We have also sought for low-energy ($\omega \lesssim 0.1$ eV) features argued as ‘charged magnons’ [10] in our calculated results. We however could not find any indications: there are many low-energy eigenstates but none of them has nonzero spectral weight. Interestingly, we find that, if we introduce a local lattice displacement, a small weight appears at the low energies, which might suggest the relevance of phonon-assisted processes.

Finally, let us discuss the controversy in the valence state of V ions in NaV$_2$O$_5$ at $T > T_c$: recent X-ray structural analyses [3] and NMR measurements [2] seem to suggest the uniform valence of V$^{4.5+}$, the system being the coupled uniform ladders with no charge disproportionation, which apparently contradicts our results shown above. However, we immediately notice that, if the dynamical fluctuation of the valence state of V ions is assumed, a possible way of reconciliation is to take into account the difference in the time scale of the measurements: if the charge (or valence) fluctuation of V ions is slow compared with the frequency of electric field of light used in the optical measurements, one finds the system to be charge-disproportionated, but if the charge fluctuation is fast enough compared with the time scales of the NMR measurement (an order of 1–100 MHz) and other structural analysis experiments, one finds the system to be uniform. It is reported that an ESR experiment of up to 24 GHz finds no motional narrowing of the linewidth [9] and that the optical measurement down to the lowest frequency of $\sim 10$ cm$^{-1}$ detects no anomalous behaviors indicating resonances [10]. We would thus suggest that measurements of frequency range of $\sim 50$ GHz to $\sim 1$ THz should be able to detect the resonant charge fluctuation in this material. Precise characterization of the charge fluctuations at $T > T_c$ needs to be made further from both experimental and theoretical sides to clarify the mechanism of the phase transition of NaV$_2$O$_5$ at $T = 34$ K.

In summary, we have calculated the optical conductivity of the trellis lattice $t$-$J$ model at quarter filling using an exact-diagonalization technique on small clusters and considered the valence state of V ions of NaV$_2$O$_5$. We have shown that the experimental features observed at $\omega \sim 0.6–2.5$ eV, including the positions of the main peak and its shoulders, anisotropy in the spectral weight, etc., can be reproduced in reasonable range of parameter values, only by assuming that the system is in the charge disproportionated ground state. We have discussed the possible reconciliation with experimental data suggesting the presence of uniform ladders.

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Fig. 4. Same as Fig. 2 but for the case with $\Delta \neq 0$. Here we assume that the sites corresponding to V$^{5+}$ ions on the zigzag structure of ordered electrons [12, 13] have a nonzero value of $\Delta$. Values of the ladder parameters of Set A are used.

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