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Temperature dependence of optical spectral weights in quarter-filled ladder systems

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The temperature dependence of the integrated optical conductivity $I(T)$ reflects the changes of the kinetic energy as spin and charge correlations develop. We calculated $I(T)$ in the frame of a t-J-V model for ladder systems, such as α'-NaV_2O_5, and show that the measured strong T dependence of $I(T)$ for NaV_2O_5 can be explained by the destruction of short-range antiferromagnetic correlations. Thus $I(T)$ provides detailed information about the T dependence of superexchange energy and thereby allows for an independent determination of magnetic energy scales.

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The integrated optical conductivity (IOC) provides a unique way to explore kinetic properties of strongly correlated systems. For discrete lattice models, usually employed to describe transition metal oxides, the IOC sum rule[1] depends upon the kinetic energy contributions $H^{\boldsymbol{\delta}}_{\rm kin}$ Eq. (2) and the projections of the different hopping vectors $\boldsymbol{\delta}$ on the polarization axis α

$$I_\alpha(T)=\int_0^\infty d\omega\,\sigma_\alpha(\omega)=\frac{\pi}{2N}\sum_{\boldsymbol{\delta}}\,\delta^2_\alpha\langle -H^{\boldsymbol{\delta}}_{\rm kin}\rangle. \quad (1)$$

Hence this allows to measure the hopping contributions along $\alpha || a,b,c$ directions separately. This option is particularly useful for anisotropic systems, such as the quarter-filled ladder compounds NaV_2O_5 (Refs. 2 and 3) and LiV_2O_5 (Ref. 4) but also in orbital ordered crystals like, e.g., $LaVO_3$ and YVO_3,[5] which all show highly anisotropic optical spectra. The T dependence of IOC provides important insight into the interplay of kinetic energy and interactions in processes of spin, charge, and/or orbital ordering.

Our work is motivated by a recent study of the optical properties of NaV_2O_5 by Presura *et al.*,[6] who observed a reduction of $I(T)$ by 12–14% between 4 K and room temperature. They proposed a fitting formula for the optical conductivity (integrated up to 2.25 eV) $I(T)/I(0)=[1-f\times\exp(-E_0/T)]$ with $f\sim 0.35(0.47)$ and $E_0\sim 286(370)$ K for $a(b)$ polarization, respectively, predicting a reduction of almost 50% for b polarization at several hundred degrees centigrade. As the main absorption is near 1 eV one may wonder about the origin of such a strong change of kinetic energy at low temperatures.

A key feature of NaV_2O_5, closely related to its charge dynamics,[7] is the three-dimensional (3D) charge ordering transition at 34 K (Ref. 8) which is accompanied by the opening of a spin gap.[9] The precise structure of the low-T phase is still under debate.[10] As discussed below, the charge fluctuations of a single ladder can be mapped onto the Ising model in a transverse field (IMTF).[11] It has been pointed out in Refs. 11 and 12 that the parameters for NaV_2O_5 are such that the IMTF is close to its quantum critical point. The corresponding soft charge excitations appear at $q_b=\pi$ and therefore do not directly contribute to $\sigma(\omega)$. If in addition the coupling to spin degrees of freedom is considered, the soft charge excitations contribute a small absorption continuum in $\sigma_a(\omega)$ within the charge gap,[12] and thus may explain the anomalous absorption observed by Damascelli *et al.*[2] Presura *et al.*[6] suggested that the low energy excitations at $q_b=\pi$ may also explain the 30 meV activation energy for charge transport,[13] which is surprisingly low in view of the 0.8 eV optical gap. Furthermore it was conjectured[6] that these excitations may cause the T dependence of IOC's and hence E_0 in the Presura *et al.* fit should measure the charge gap.

The picture which evolves from our calculations is different. The kinetic energy of the IMTF does not show any significant temperature dependence which could be attributed to E_0. The temperature scale of the variation of the kinetic energy is set by the bare Coulomb interaction. The t-J-V model, however, in agreement with the experimental data, displays a dramatic decrease of kinetic energy in the range $0.2J<T<J$, where J is the exchange integral[14,15] (order of 0.1 eV) of the effective one-dimensional (1D) Heisenberg model which describes the spin dynamics of NaV_2O_5.[9] We attribute the large decrease of $I(T)$ to the destruction of short range antiferromagnetic (AF) correlations by thermal population of local triplet excitations. Thereby IOC's allow us to measure the superexchange contribution to $E_{\rm kin}$.

At quarter filling, NaV_2O_5 can be described by a t-J-V model,[16–18] as the hopping matrix elements $t_{\mathbf{ij}}$ between vanadium d_{xy} orbitals are small compared with the Hubbard interaction of vanadium ($U\sim 4$ eV):

$$H=\sum_{\boldsymbol{\delta}} H^{\boldsymbol{\delta}}_{\rm kin}+\sum_{\langle i,j\rangle} J_{\mathbf{ij}}\left(\mathbf{S_i}\cdot\mathbf{S_j}-\frac{n_{\mathbf{i}}n_{\mathbf{j}}}{4}\right)+\sum_{\langle\mathbf{i},\mathbf{j}\rangle} V_{\mathbf{ij}}n_{\mathbf{i}}n_{\mathbf{j}}, \quad (2)$$

with $H^{\boldsymbol{\delta}}_{\rm kin}=-\Sigma_{\mathbf{i}\sigma}t_{\boldsymbol{\delta}}(\tilde{c}^\dagger_{\mathbf{i},\sigma}\tilde{c}_{\mathbf{i}+\boldsymbol{\delta},\sigma}+\text{H.c.})$. Elimination of local double occupancies yields the Heisenberg term with $J_{\mathbf{ij}}=4t^2_{\mathbf{ij}}/U$ (Ref. 19) and constrained electron creation operators $\tilde{c}^\dagger_{\mathbf{i},\sigma}=c^\dagger_{\mathbf{i},\sigma}(1-n_{\mathbf{i},-\sigma})$, which enter the densities $n_{\mathbf{i}}=\Sigma_\sigma\tilde{c}^\dagger_{\mathbf{i},\sigma}\tilde{c}_{\mathbf{i},\sigma}$ in the Coulomb repulsion ($V_{\mathbf{ij}}$) between neighbors (Fig. 1). $\mathbf{S_i}$ is the spin-$\frac{1}{2}$ operator at site $\mathbf{i}$. The sums are

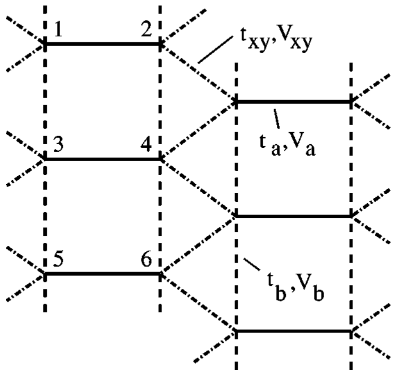

FIG. 1. Trellis lattice describing the positions of vanadium ions in the (a,b) plane of α'-NaV_2O_5.

over spin $\sigma=\uparrow,\downarrow$ and all neighbor bonds $\langle \mathbf{i},\mathbf{j}\rangle$ on the trellis lattice, depicted in Fig. 1. Typical parameters values are included in Fig. 3.

We begin with the investigation of charge fluctuations in the spinless case. Due to the interactions V_{ij} this is a nontrivial problem, which can be simplified to a single ladder model without changing the essence of the problem, provided V_{xy} and t_{xy} are not too large. For large $U/|t_{\mathbf{ij}}|$ and $V_a/|t_{\mathbf{ij}}|$ the relevant subspace of one electron per rung can be represented by pseudospin operators $\mathbf{T}_r$, where the eigenvalues $\pm\frac{1}{2}$ of T_r^z correspond to the left/right position of the electron within the rung r, and one obtains the 1D IMTF:[11]

$$H_{\rm ladder}=-2t_a\sum_r T_r^x+2V_b\sum_r T_r^zT_{r+1}^z. \tag{3}$$

Here the Ising interaction, due to Coulomb repulsion, favors zigzag charge correlations on the ladder, while the kinetic energy $E_{\rm kin}$ ($\propto t_a$) appears as a transverse field opposing these correlations.

The 1D IMTF is exactly solvable.[20] The kinetic energy, expressed in terms of the dimensionless parameter $h=2t_a/V_b$, is given by

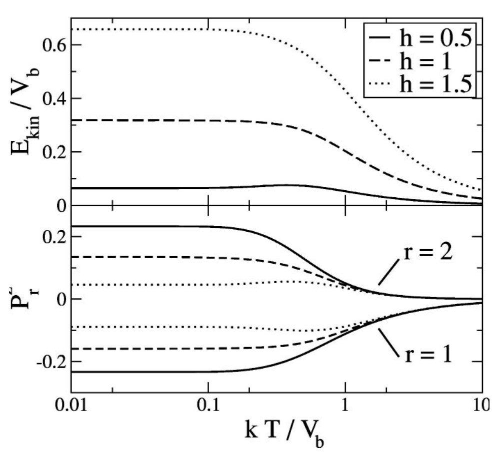

FIG. 2. Temperature dependence of the kinetic energy (top) and pseudospin CF derived from the exact solution of the IMTF for $h=2t_a/V_b=0.5$, 1.0, and 1.5.

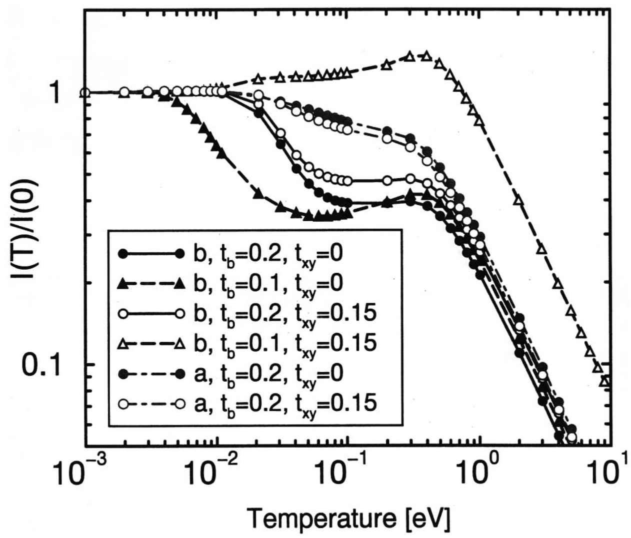

FIG. 3. IOC for a (dot-dashed) and b polarization (solid and dashed lines). Results are given for both $t_{xy}=0.15$ (open) and $t_{xy}=0$ (filled symbols). Common parameters are $t_a=0.4$, $V_a=V_b=0.8$, and $V_{xy}=0.9$ eV. The set $t_b=0.2$ and $t_{xy}=0.15$ corresponds to spectra shown in Ref. 12.

$$\frac{E_{\rm kin}}{V_b}=\frac{h}{2\pi}\int_0^{\pi}dk\,\frac{\cos k+h}{\epsilon(k)}\tanh\left(\frac{\beta V_b\epsilon(k)}{2}\right), \tag{4}$$

where $\beta=1/k_BT$ and $\epsilon(k)=\sqrt{h^2+2h\cos k+1}$ is the quasiparticle dispersion which becomes soft at $k=\pi$ as $h\rightarrow 1$ (i.e., $E_0=V_b\epsilon(\pi)=|2t_a-V_b|$).

Figure 2 shows the temperature dependence of the exact results for $E_{\rm kin}$ and the pseudospin correlation functions (CF's) $P_r=(1/N)\Sigma_{r'}\langle T_{r'}^zT_{r'+r}^z\rangle$ for nearest and next-nearest neighbors ($r=1,2$). Obviously, the temperature dependence of $E_{\rm kin}$ and the CF's is dictated by the bare interaction V_b as only T scale, provided $t_a \not\gg V_b$. The CF's decrease gradually with increasing $h=2t_a/V_b$, and vanish only in the limit $h\rightarrow\infty$. We note one peculiarity of the exact solution: for $h<1$ the magnetization $\langle T_r^x\rangle\propto E_{\rm kin}$ is not strictly monotonic in temperature. Here $\langle T_r^x\rangle$ profits from a decrease of z correlations. In the high temperature limit one finds $E_{\rm kin}\sim h/T$.

From Fig. 2 we conclude that the charge-only model cannot explain the decline of $I(T)$ below room temperature. To study the problem including spin there are two alternatives: (i) the complete spin-pseudospin model[11,12] and (ii) the t-J-V model which we shall choose.

For the calculation of the optical spectra and IOC's for the t-J-V model we employ, as in Ref. 12, the finite temperature Lanczos technique developed by Jaklič and Prelovšek.[21] The exact diagonalization (ED) was performed for a 4×4 site system. As we are studying an insulator, we can restrict the calculation of $\sigma_\alpha(\omega)$ to the finite frequency response given by the Kubo formula

$$\sigma_\alpha(\omega)=\frac{1-e^{-\beta\omega}}{\omega}\,{\rm Re}\int_0^{\infty}d\tau\, e^{i\omega\tau}\langle j_\alpha(\tau)j_\alpha\rangle, \tag{5}$$

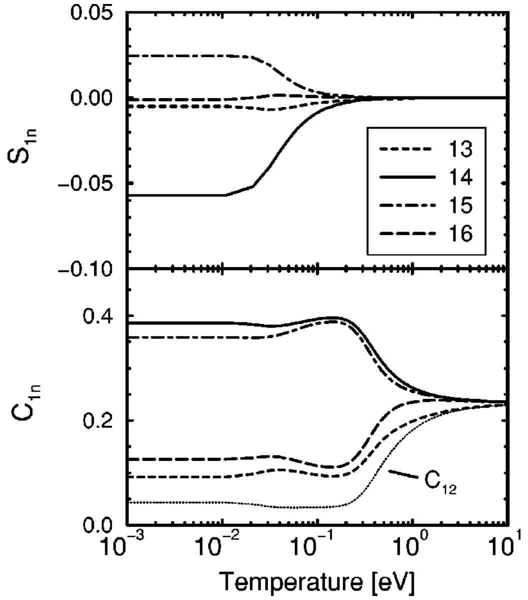

FIG. 4. Spin $S_{1n}=\langle S_1^z S_n^z\rangle$ (top) and charge correlations $C_{1n}=\langle n_1 n_n\rangle$ (bottom) (labels see Fig. 1), as function of temperature ($t_b=0.2$, $t_{xy}=0.15$).

where $j_\alpha = i\Sigma_{\langle\mathbf{i},\mathbf{j}\rangle,\sigma} t_{\mathbf{ij}}\delta_\alpha^{\mathbf{ij}}(\tilde{c}_{\mathbf{i},\sigma}^\dagger \tilde{c}_{\mathbf{j},\sigma} - \text{H.c.})$ is the $\alpha(=a,b)$ component of the current operator and $\delta_\alpha^{\mathbf{ij}}$ denotes the α component of the vector connecting sites **i** and **j**. In the following, energies and temperature are given in eV.

Figure 3 displays the temperature variation of $I(T)$ for the t-J-V model for several sets of parameters on a log-log scale. The data show a strong decrease at low temperature, which is particularly pronounced for b polarization, while the decrease of the kinetic energy at high temperatures ($T \gtrsim V_b$) is similar to that discussed for the pseudospin (charge only) model. The low-T variation is controlled by the magnetic exchange $J \propto t_b^2/V_a$ as can be seen by comparing the data for $t_b=0.1$ and 0.2 eV. The results for $t_{xy}=0$ and $t_{xy}=0.15$ are similar (for $t_b=0.2$) (Ref. 22) which is consistent with the suppression of superexchange related to t_{xy}, as discussed in Ref. 14.

The near-neighbor spin CF's S_{1n} for $t_b=0.2$ and $t_{xy}=0.15$ are shown in Fig. 4. The comparison with the kinetic energy for these parameters (open circles in Fig. 3) clearly illustrates that the low temperature decrease in E_{kin} is due to the loss of short-range AF spin correlations, whose T variation is controlled by the magnetic exchange J. The largest spin CF's at low temperatures are S_{14} and S_{15} consistent with *zigzag charge correlations*, i.e., large C_{14} and C_{15}. As discussed along with Fig. 2, the short-range charge correlations, however, exist up to higher temperatures, determined by V_b.

Finally, the smallness of C_{12} below $T \lesssim 0.4$ supports the validity of the pseudospin model, where only one electron per rung is allowed for. We also note that the data for C_{1n} are consistent with the pseudospin correlation P_r, shown in Fig. 2.

We emphasize that the kinetic energy is essentially determined by short-range spin correlations. In the insulating state E_{kin} has two major contributions which lead to the two distinct T scales in Fig. 3: (i) valence fluctuations, which have been discussed already in the context of the pseudospin model, and (ii) virtual excitations, which give rise to magnetic superexchange whose T variation is controlled by J.

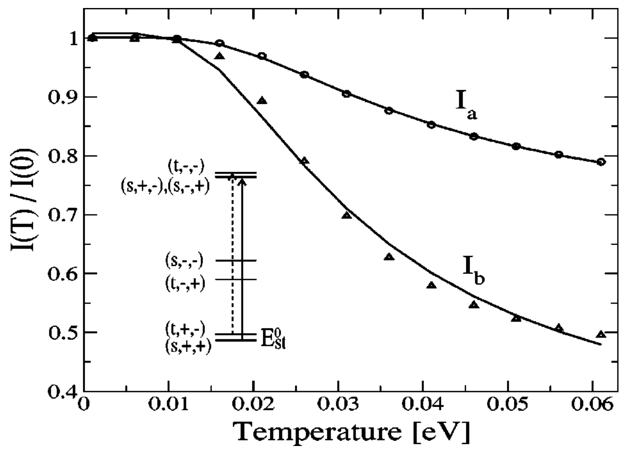

FIG. 5. IOC for standard parameters with $t_b=0.2$ and $t_{xy}=0.15$ eV: Fit (solid lines) as described in the text and ED from Fig. 3 (symbols). Inset: Sketch of optical excitations of the two-rung model. For b polarization the triplet transition matrix element is zero (dashed).

To understand the low-T behavior of IOC's it is revealing to study a two-rung system including all terms in Eq. (2), except t_{xy} and V_{xy}, and to employ the spectral representation of $I(T)$ [Eq. (1)]:

$$I(T)=\frac{\pi}{Z}\sum_n e^{-\beta E_n}\sum_{\substack{m\\E_m>E_n}}\frac{1-e^{-\beta(E_m-E_n)}}{E_m-E_n}|\langle m|j_\alpha|n\rangle|^2, \tag{6}$$

where the summation is over eigenstates of H and Z is the partition function. The eigenstates are characterized by (S,p_a,p_b), i.e., total spin [$S=$singlet (triplet)] and parity $p_{a(b)}$ in the $a(b)$ direction. The level scheme is sketched in Fig. 5. The ground state $(s,+,+)$ is a fully symmetric singlet. The lowest excited states are the triplet states $(t,+,-)$ and $(t,-,+)$, where $(t,+,-)$ is lower in energy, as it is composed of bonding and antibonding orbitals in the a direction, while $(t,-,+)$ consists of orbitals in the b direction and lies already ≈ 400 meV above the ground state. Its thermal population in Eq. (6) can be neglected at low T. The difference between the two polarizations is due to the fact that the current operators j_α conserve the symmetries (S,p_a,p_b), except for $p_\alpha \to -p_\alpha$. One finds that j_b has non-vanishing matrix elements between the ground state and the first excited singlet with $(s,+,-)$, whereas the matrix elements involving $(t,+,-)$ vanish. This has the important consequence that the triplet state $(t,+,-)$ contributes to Z but not to the numerator of the Kubo formula [Eq. (6)], leading to

$$I_b(T)\propto\frac{1-e^{-\beta\Delta E_s}}{\Delta E_s}\frac{1}{1+3e^{-\beta E_{\text{st}}^0}}. \tag{7}$$

Here the factor of 3 reflects the degeneracy of the triplet and ΔE_s is the energy difference between the lowest singlet states. The situation is different for *a* polarization, where also $(t,-,+)$ contributes, resulting in an extra term

$$I_a(T) \propto \frac{1-e^{-\beta\Delta E_s}}{\Delta E_s(1+3e^{-\beta E_{\rm st}^0})} + 3\kappa \frac{1-e^{-\beta\Delta E_t}}{\Delta E_t(3+e^{\beta E_{\rm st}^0})}, \qquad (8)$$

where κ is a ratio of matrix elements. In both cases the low-*T* behavior is governed by local singlet-triplet excitations of energy $E_{\rm st}^0$ and hence by the exchange integral $J\,(=E_{\rm st}^0)$ of the effective one-dimensional Heisenberg model $H=J\Sigma \mathbf{S}_r\cdot\mathbf{S}_{r+1}$.[14,16] The influence is, however, different for *a* and *b* polarization. The *T* dependence via the optical excitation energies ΔE_s and ΔE_t (~ 1 eV) is marginal at low *T*.

We infer that also in extended systems, the low-*T* behavior is due to local singlet-triplet excitations with energy, as estimated from the two-rung formula, $\tilde{E}_{\rm st}^0 = 4t_b^2/[(V_a+V_b)\sqrt{1+4(t_a/V_b)^2}]$ for $V_a, V_b \gg t_a, t_b$. For the standard parameters and $t_b=0.2$, $\tilde{E}_{\rm st}^0 \sim 70$ meV.

As the results of the two-rung system are mainly determined by symmetry arguments and energy-scale separation, we consider the expressions in Eqs. (7) and (8) as generic results with system-dependent parameters: $E_{\rm st}^0$, κ, ΔE_s, and ΔE_t. We have determined these parameters by fitting the exact diagonalization data of the 4×4 system (Fig. 3) resulting in $E_{\rm st}^0 \sim 76\,(61)$ meV for *a* (*b*) polarization, respectively, and $\kappa \sim 0.54$. The fit value for $E_{\rm st}^0$ agrees well with the estimate $\tilde{E}_{\rm st}^0$. The fit curves along with the ED data are shown in Fig. 5.

A similar fit of the experimental data in (Ref. 6) yields $J\sim 39$ meV, consistent with values obtained from other experiments, e.g., $J\sim 48.2$ (Ref. 9) and 37.9 meV.[15,23,24] According to $\tilde{E}_{\rm st}^0$ we estimate $t_b \sim 0.15$, such as in Refs. 14 and 16 instead of 0.2 eV used in this study and in Ref. 12.

Finally one may wonder about the change of $E_{\rm kin}$ at the 34 K transition.[9] As this charge order transition indicates the onset of 3D long-range order, there is not necessarily a large change of short-range correlations to be expected. This view is consistent with the small change of $I(T)$ at 34 K in the Presura *et al.* data.

In conclusion, we have found for the quarter-filled *t-J-V* model, in agreement with experimental data, a large decrease of IOC's in the temperature range $0.2J < T < J$ ($\sim 50\%$ for *b* polarization). This dramatic change in kinetic energy is magnetic in origin, and is explained by the destruction of short-range spin correlations as *T* is increased. Moreover, we have shown that the nearly quantum critical valence fluctuations in this system do not contribute to the variation of IOC at low temperature.

We argue, therefore, that the observed *T* dependence of optical spectral weights in α' NaV_2O_5 is explained by the decrease of the magnetic superexchange. This underlines the potential of optical experiments to infer the magnetic exchange *J* from the *T* dependence of the spectra and to explore quantitatively the changes of the kinetic (and superexchange) energy in correlated systems (particularly in systems with small *J*), which cannot be achieved otherwise.

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