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Nature of insulating state in NaV$_2$O$_5$ above charge-ordering transition: A cluster dynamical mean-field study

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The nature of the insulating state driven by electronic correlations in the quarter-filled ladder compound $\alpha$NaV$_2$O$_5$ is investigated within a cluster dynamical mean-field approach. An extended Hubbard model with first-principles tight-binding parameters has been used. It is shown that the insulating state in the charge-disordered phase of this compound is formed due to the transfer of spectral density and dynamical charge fluctuations where for the latter, the role of intersite Coulomb interaction is found to be of crucial importance.

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The ladder compound NaV$_2$O$_5$ has been a subject of great interest over the last five years. It exhibits a remarkable phase transition at $T_c = 34$ K, now identified as charge-ordering of the zigzag type. The first interpretation of this phenomenon was related to a model of different V$^{4+}$ and V$^{5+}$ chains and associated with the spin-Peierls transition in V$^{4+}$ chains. However, recent experiments show that above $T_c$, all vanadium ions are equivalent (V$^{4.5+}$), whereas below $T_c$, a charge disproportionation appears. Analysis of the additional experimental data on the microwave dielectric susceptibility, entropy change at $T_c$, and magnetic-field effect on $T_c$ has led to an unambiguous conclusion about zigzag charge ordering (for a review, see Ref. 9).

Both the charge-ordered phase and charge-disordered one are insulating with an energy gap of the order of 0.8–1 eV. The presence of the gap in the ordered phase is not surprising and it was reproduced successfully, for example, in the recent local-density approximation (LDA)+$U$ calculations. The properties of the disordered phase are much more difficult to understand. In contrast to the isostructural ladder compound CaV$_2$O$_5$, NaV$_2$O$_5$ has a quarter-filled band rather than a half-filled one and cannot be considered as a standard Mott insulator. It has been proposed in Refs. 5 and 6 that a large value of the transverse hopping parameter in the ladder which splits the band into sub-bands of the bonding and antibonding states could be responsible for the Mott insulator behavior in NaV$_2$O$_5$ in the presence of strong Coulomb interactions. However, it is not known whether this mechanism is adequate for the realistic values of the parameters characterizing the single-particle electronic structure and the electron-electron correlations.

In this paper we investigate the correlation effects in NaV$_2$O$_5$ taking into account nonlocal dynamical charge fluctuations on the rung for this two-leg ladder compound. This allows us to understand the origin of the insulating state above $T_c$ and to estimate the relative importance of various physical mechanisms responsible for the gap formation.

The crystal structure of NaV$_2$O$_5$ projected in the $xy$ plane is sketched in Fig. 1. The results of the x-ray, NMR, and optical experiments as well as the Hartree-Fock calculations support the zigzag charge-ordering state for low temperatures (see Fig. 1). In this state one has approximately one $d$ electron per rung of the vanadium ladder. We start with LDA+$U$ (Ref. 13) calculations of the ordered states but, in contrast to the previous work, we considered several different types of the charge ordering. This gives us an opportunity to estimate the on-site and intersite Coulomb interactions $U$ and $V$.

It is natural to assume that the tendency to keep the number of $d$ electrons per rung close to unity also takes place above the transition temperature leading to strong short-range order and well-developed dynamical charge fluctuations. This is confirmed by the temperature dependencies of the spin gap and the entropy measurements. Usual LDA as well as the mean-field theories such as Hartree-Fock or...
LDA+$U$ methods are insufficient to take into account these essential many-body processes. The simplest reliable way to consider such short-ranged correlation effects is the use of the dynamical mean-field theory (DMFT),\textsuperscript{14} which can be combined with realistic LDA band-structure calculations (LDA+DMFT).\textsuperscript{15,16} The DMFT maps the initial many-body problem for a crystal onto a self-consistent quantum-impurity problem. To consider the phenomena such as charge ordering or fluctuations, the intersite correlations are of crucial importance, therefore we need to use a cluster generalization of the DMFT method.\textsuperscript{17,18} This extended DMFT scheme has been successfully applied for low-dimensional systems such as two-dimensional high-temperature superconductors\textsuperscript{18,19} and quasi-one-dimensional organic conductors.\textsuperscript{20} The most reasonable choice of the cluster in our case is a pair of vanadium atoms at the rung (see Fig. 1), because the hopping between V ions inside the rung ($t_d$) is much larger, two to four times (see Ref. 2 and downfolding results below in the text) the corresponding values for ions in different rungs ($t_\perp$ and $t_\parallel$, Fig. 1). With this cluster we can treat the strongest in-run interaction rigorously and much weaker interrun interaction via dynamical mean-field approximation. With the in-run interaction being a few times stronger than the interrun one, the choice of the rung as a free cluster is a natural one and we do not expect strong finite-size effects with increasing size of the cluster.

We use the extended Hubbard model for a two-leg ladder:

$$H = \sum_{ij} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \sum_i U_i n_{i\uparrow} n_{i\downarrow} + \sum_{i<j} V_{ij} n_{i\sigma} n_{j\bar{\sigma}},$$

(1)

where $t_{ij}$’s are the effective hoppings, and $U_i$ and $V_{ij}$ are local and intersite Coulomb interactions respectively, $n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma}$. The proper choice of hopping parameters is not simple, and the most widely used set ($t_\perp = 0.38$ eV, $t_\parallel = 0.18$ eV, $t_1^z = 0.012$ eV, $t_2 = 0.03$ eV) was obtained by fitting to the LDA bands.\textsuperscript{2} Recently a rigorous procedure of a massive downfolding of LDA bands to a few-band description and the subsequent Fourier transformation of the resulting Hamiltonian from reciprocal to direct space to extract the single-electron parameters has been developed within the framework of a linear-muffin-tin-orbital (LMTO) description.\textsuperscript{21} This method applied to NaV$_2$O$_5$ gave the following set of hopping parameters: $t_\perp = 0.398$ eV, $t_\parallel = 0.084$ eV, $t_1 = 0.025$ eV, and $t_2 = 0.022$ eV which is rather close to the standard one presented above, but in addition the diagonal (Fig. 1) hopping parameter $t_d = 0.083$ eV is appreciable, which was independently pointed out by Yaresko \textit{et. al.} \textsuperscript{11} and also by Valenti \textit{et. al.} \textsuperscript{22} for the related LiV$_2$O$_5$ compound. We have found that these diagonal hopping processes are very important. As can be see in Fig. 2, the inclusion of diagonal hopping $t_d$ in the single-electron part of the model Hamiltonian provides a much better agreement of the bare DOS with the LDA.

The values of the on-site $U$ and intersite $V$ Coulomb interaction parameters were determined from LDA+$U$ calculations using the following scheme. The LDA+$U$ functional gave few different solutions corresponding to the different geometry of charge ordering for the different $d$-electron per two $V$ ions. The two types of V ions in such solutions have a different number of the $d$-electrons $n_d$ and different $d$-orbital energies. From the five $d$-orbitals of the V ion in the NaV$_2$O$_5$ crystal structure, one orbital ($d_{xy}$) is strongly split from the others and a partially filled band is formed almost exclusively by this orbital. We have mapped the results of our LDA+$U$ calculations on the one-orbital-per-V-site model with on-site $U$ and effective in-rung intersite $V$ Coulomb parameters. This effective $V$ is a combination of the real in-rung $V_{\text{rung}}$ and diagonal interrung $V_{\text{diag}}$ parameters $V = V_{\text{rung}} - 2V_{\text{diag}}$. The ratio of the $d$-orbital energy splittings for two types of V ions-to the value of the difference of the $d_{xy}$-orbital occupation numbers for the ground-state zigzag charge ordering, by definition, is equal to $U$ while that ratio for the charge ordering with one rung empty and one rung fully occupied is $U + V$. From that we obtained the following values: $U = 2.8$ eV and $V = 0.17$ eV. While the $U$ value is close to the estimations for vanadates by other methods, the $V$ value is too small. We must note that the mapping of the LDA+$U$ calculations on the model scheme is not uniquely defined. If instead of the difference in the occupancies of the $d_{xy}$ orbitals on two types of the V ions one takes the difference of the total $d$-shell occupation numbers, then the $V$ value would be much larger (1.28 eV). So 0.17 eV and 1.28 eV can be regarded as the lower and upper bounds for the estimation of the $V$ value. In the following we used two $V$ values: the lowest 0.17 eV and the value 0.5 eV which is about half way between the lower and upper bounds.

The crystal Green-function matrix in the LDA+DMFT approach can be written as

$$G(k,i\omega) = \left[(i\omega + \mu)\mathbf{1} - \mathbf{h}(k) - \Sigma(i\omega)\right]^{-1},$$

(2)

where $h_{\alpha\beta}(k)$ is the effective hopping matrix, $\Sigma_{\alpha\beta}(i\omega)$ is the self-energy matrix of the two-site supercell dimension which is assumed to be local, i.e., $k$ independent, and $\mu$ is the chemical potential.
In the paramagnetic case we can transform $T_{ij}$ where the orbital energy matrix for the conduction band $E_{ij}$ describes effective interactions with the rest of the crystal:

$$G^{-1}(i\omega) = G^{-1}(i\omega) + \Sigma(i\omega),$$

where the local cluster Green-function matrix is equal to $G_{ab}(i\omega) = \sum_{s} G_{sab}(\vec{k}, i\omega)$, and the summation runs over the Brillouin zone of the lattice.

We used the exact diagonalization (ED) scheme to solve the cluster DMFT problem. In this case the lattice Hamiltonian is mapped onto the finite cluster-impurity model:

$$H_{imp} = \sum_{i,j,\sigma} T_{ij} c_{i\sigma}^+ c_{j\sigma} + \sum_i U n_{i\uparrow} n_{i\downarrow} + \sum_{i,j,\sigma} V_{ij} n_{i\sigma} n_{j\sigma}$$

$$+ \sum_{k,i,j,\sigma} E_{ij\sigma}(k) a_{k\sigma}^+ a_{k\sigma}$$

$$+ \sum_{k,i,j,\sigma} \Gamma_{ij\sigma}(k)(a_{k\sigma}^c e^{i\sigma} + \text{H.c.}),$$

where $T_{ij}$ are the hopping parameters inside the cluster (for our two-site rung cluster this is only $t_\perp$), and $E_{ij\sigma}(k)$ and $\Gamma_{ij\sigma}(k)$ are effective energies and the hybridization matrix for finite-chain bath orbitals $k=1, \ldots, n_b$, respectively.

For the iterative solution of the effective impurity model Eq. (4) we use the Lanczos version of the ED method. The orbital energy matrix for the conduction band $E_{ij\sigma}(k)$, and the corresponding hybridization matrix $\Gamma_{ij\sigma}(k)$, are the effective parameters which reproduce the bath Green function:

$$G^{-1}(i\omega_n) = (i\omega_n + \mu)^* 1 - T - \sum_k \Gamma_k[i\omega_n - E_k]^{-1} \Gamma_k^+.$$ 

In the paramagnetic case we can transform $G$, $T$, $\Gamma_k$, and $E_k$ matrices of the dimension $2 \times 2$ for our cluster to the diagonal $\text{bonding-antibonding}$ basis $\lambda = \{b,a\}$. In this case $T_\lambda = \{-t_1,t_1\}$ and $G_\lambda = \{G_b, G_a\}$, where $G_{b,a} = G_{11} \pm G_{12}$. We used ten bath orbitals for our two-site cluster.

The parameters $\{E_{ij\sigma}, \Gamma_{kij}\}$ are now fitted to reproduce the bath Green function $G_{\lambda \sigma}(i\omega_n)$ for bonding and antibonding states independently. The next step is the solution of the cluster-impurity problem [Eq. (4)] to get the cluster self-energies $\Sigma_{ij\sigma}(i\omega_n)$ which are required for the next DMFT iterations. After solving the effective cluster problem using the Lanczos algorithm, the local Green’s-function matrix $G_{ij\sigma}(i\omega_n)$ was determined and the cluster self-energy $\Sigma_{ij\sigma}(i\omega_n)$ was obtained within the cluster-impurity scheme [Eq. (3)].

The phase diagram obtained in our DMFT calculations is shown in Fig. 3. One can see that for large enough $U$ and realistic values of $V$ the disordered state turns out to be insulating. This arises from the two physically different mechanisms. The first one is the spectral density transfer which can effectively change the quarter-filled system into the half-filled one. For large enough $U$ the energy band splits into Hubbard sub-bands with the average spectral weight one-half for each of them and therefore the system appears to be insulator for half-filling instead of complete filling. In this large-$U$ limit the extended Hubbard model reduces to a so-called $t$-$J$-$V$ model which can explain insulating properties and optical spectra of NaV$_2$O$_5$. Our calculations do show a formation of the lower and upper Hubbard bands which leads to the spectral density transfer and moves the Fermi energy into the pseudogap between bonding and anti-bonding states in the lower Hubbard band as it was proposed qualitatively in Refs. 5 and 6. However, the gap which can be obtained due to this mechanism is very small. To increase its value (consistent with the experiment) the inclusion of the inter-site Coulomb repulsion ($V$) appears to be important (Fig. 4). Our calculations show that the broad enough gap arises with the increase of $V$ suddenly, as a result of a first-order phase transition. With $V=0$ the insulator is stable only for $U \approx 4$ eV and above, while the already small value of $V = 0.1$ eV decreases the critical $U$ value below 3 eV.
results of LDA+U calculations even for the lowest bounds for \( V \) gave a point in the phase diagram (the cross in Fig. 3) which is well above the metal-insulator transition line. It is important to stress that if one carries out the calculation in a usual single-site DMFT calculation instead of the cluster DMFT an adequate description of the electronic structure is not obtained for the same values of the parameters, and the insulating states appear only for \( U > 12 \) eV! This demonstrates the crucial importance of the charge fluctuations on the rung for the formation of the insulating state in Na\( \text{V}_2\text{O}_5 \) with realistic \( U \) values. We also analyzed the structure of the ground state in the effective cluster model [Eq. (4)] and found that for our LDA+U Coulomb parameters about 70% of the ground-state eigenfunction corresponds to the configurations with one electron per rung and 20% is related to empty rung states. This means that the configurations with the empty rungs in Na\( \text{V}_2\text{O}_5 \) have also appreciable weight.

We conclude that the insulating state of Na\( \text{V}_2\text{O}_5 \) above \( T = 34 \) K is characterized by strong dynamical charge fluctuations. In this respect the situation is close to the half-filled Hubbard chain or a pseudospin-liquid-like phase: the tendency for the formation of the state with one electron per rung is similar to the singlet state formation in strongly frustrated spin systems and can be described in the limit of large \( U \) and \( V \) by an anisotropic Heisenberg-like model.\(^{5,10,25,26}\) It is important to stress that experimentally the spin gap exists also above \( T_c \).\(^{12}\) However, this description is only qualitative.

Our calculations demonstrate that this compound is situated near the boundary between metal and insulator states and should be described by itinerant-electron models rather than by localized-electron ones. Since the metal-insulator transition in the model under consideration turns out to be strongly first-order type, the gap is not small. The value of the gap depends strongly on the intersite Coulomb repulsion parameter \( V \), as is demonstrated in Fig. 4. One can see that solution with \( V = 0.5 \) eV has a gap value which is in much better agreement with the experimental value (0.8–1.0 eV, Ref. 3) than that for \( V = 0.17 \) eV. The insulating properties cannot be described correctly neglecting the charge fluctuations on the rung (with too small values of \( V \), or using the single-site DMFT approach instead of the cluster one).

To conclude, we present results on the cluster DMFT calculations for the insulating phase of Na\( \text{V}_2\text{O}_5 \) above the charge-ordering transition using the extended Hubbard model with first-principles tight-binding parameters. The nonlocal charge fluctuations and intersite Coulomb interaction is of crucial importance for the formation of an insulating state.

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