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 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.

The crystal structure of NaV$_2$O$_5$ projected in the $xy$ plane is sketched in Fig. 1. The results of the x-ray,$^7$ NMR,$^8$ and optical$^3$ experiments as well as the Hartree-Fock calculations$^4$ 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,$^{11}$ 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.$^{12}$ Usual LDA as well as the mean-field theories such as Hartree-Fock or

FIG. 1. Schematic representation of the crystal structure of the vanadium layers in NaV$_2$O$_5$ and various hopping integrals. The vanadium ions are denoted by filled circles. The ellipse shows the cluster which plays the role of an effective impurity in the dynamical mean-field theory (DMFT) calculations. A zigzag charge ordering of the V$^{4+}$ and V$^{5+}$ ions, obtained from our LDA+$U$ calculations as a ground state is shown on the left ladder. Bold arrows are the translation vectors.
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), which can be combined with realistic LDA band-structure calculations (LDA+DMFT). 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. This extended DMFT scheme has been successfully applied for low-dimensional systems such as two-dimensional high-temperature superconductors and quasi-one-dimensional organic conductors. 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 ($t_\perp$) 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 $t_d$, Fig. 1). With this cluster we can treat the strongest in-rung interaction rigorously and much weaker interrung interaction via dynamical mean-field approximation. With the in-rung interaction being a few times stronger than the interrung 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:

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

where $t_{ij}$'s are the effective hoppings, and $U_i$ and $V_{ij}$ are local and interrung 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, $t_d = 0.18$ eV, $t_1 = 0.012$ eV, $t_2 = 0.03$ eV) was obtained by fitting to the LDA bands. 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. This method applied to NaV$_2$O$_5$ gave the following set of hopping parameters: $t_\perp = 0.398$ eV, $t_d = 0.084$ 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 et al. and also by Valenti et. al. for the related LiV$_2$O$_5$ compound. We have found that these diagonal hopping processes are very important. As can be seen 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 interrung $V$ 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 $V_{\text{diag}}$ parameters $V = V_{\text{rung}} - 2 V_{\text{diag}}$. 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 $V + U$. 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

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

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.

![FIG. 2. Bare densities of states (DOS). Solid lines correspond to LDA DOS. The dashed and long-dashed lines represent the first-principles tight-binding parametrizations without and with $t_d$ hopping, respectively.](image)
In the paramagnetic case we can transform \( G \) where
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T_{ij} \quad \text{orbital energy matrix for the conduction band}
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E_{ij} \quad \text{for finite-chain bath orbitals}
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\text{Brillouin zone of the lattice.}
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\text{our two-site rung cluster this is only}
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\text{tained from our tight-binding–LMTO calculation}
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\text{the disordered state turns out to be in-
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\text{large-U limit the extended Hubbard model reduces to a so-
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\text{we use the Lanczos version of the ED method.}
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\text{the band Green function} \ G_{\lambda\nu}(i\omega_n)
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\text{in Refs. 5 and 6. However, the gap which can be obtained}
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\text{Hubbard sub-bands with the average spectral weight one-half}
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\text{effectively change the quarter-filled system into the half-
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\text{we used ten bath orbitals for our two-site cluster.}
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\text{parameters} \ \{E_{\lambda\nu}, \Gamma_{\lambda\nu}\} \text{are now fitted to reproduce}
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\text{cluster-impurity problem}
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\[
\text{finite cluster-impurity model:}
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H_{\text{imp}} = \sum_{i,j,\sigma} \sum_{i} \sum_{i} U_{ij} n_{i\sigma} n_{j\sigma}
\]
\[
+ \sum_{k,i,j,\sigma} E_{ij\sigma}(k) a_{ki\sigma}^\dagger a_{kj\sigma}
\]
\[
+ \sum_{k,i,j,\sigma} \Gamma_{ij\sigma}(k) (a_{ki\sigma}^\dagger a_{kj\sigma} + \text{H.c.})
\]
\[
\text{where} \ T_{ij} \ \text{are the hopping parameters inside the cluster (for}
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\text{and} \ E_{ij\sigma}(k) \ \text{and}
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\text{For the iterative solution of the effective impurity model}
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\[
\text{we use the Lanczos version of the ED method.}
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\text{The orbital energy matrix for the conduction band} \ E_{ij\sigma}(k), \ \text{and}
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\text{the corresponding hybridization matrix}
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\text{For the twosite rung cluster this is only}
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\text{finite-chain bath orbitals}
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\text{effectiv}
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\[
\text{effective parameters which reproduce the bath Green func-
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\text{the paramagnetic case we can transform} \ G, \ \Gamma_k, \ \text{and} \ E_k
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\text{of the dimension} \ 2 \times 2 \ \text{for our cluster to the diago-
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\text{bonding-antibonding} \ \text{basis} \ \lambda = \{b,a\}. \ \text{In this case} \ T_{\lambda}
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\text{the lowest bounds values of} \ U \ \text{and} \ V \ \text{obtained from our LDA+U calculation.}
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\[
\text{The parameters} \ \{E_{\lambda\nu}, \Gamma_{\lambda\nu}\} \ \text{are now fitted to reproduce}
\]
\[
\text{In this case the lattice Hamiltonian is mapped onto the finite cluster-impurity model:}
\]
\[
G^{-1}(i\omega_n) = (i\omega_n + \mu)^* 1 - \sum_k \Gamma_k [i\omega_n - E_k]^{-1} \Gamma_k^+.
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\text{In the paramagnetic case we can transform} \ G, \ \Gamma_k, \ \text{and} \ E_k
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\text{the first one is the spectral density transfer which can}
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}
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 NaV$_2$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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14For a review, see A. Georges et al., Rev. Mod. Phys. 68, 13 (1996).