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Nature of insulating state in NaV_2O_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 $\alpha'\text{NaV}_2\text{O}_5$ 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_2O_5 has been a subject of great interest over the last five years.¹⁻¹² It exhibits a remarkable phase transition at $T_c=34$ K, now identified as charge-ordering of the *zigzag* type.^{2,4-8} 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.¹ However, recent experiments^{7,8} show that above T_c all vanadium ions are equivalent ($\text{V}^{4.5+}$), 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.³ 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.¹¹ The properties of the disordered phase are much more difficult to understand. In contrast to the isostructural ladder compound CaV_2O_5 , NaV_2O_5 has a quarter-filled band² 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 states² could be responsible for the Mott insulator behavior in NaV_2O_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_2O_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_2O_5 projected in the xy plane is sketched in Fig. 1. The results of the x-ray,⁷ NMR,⁸ and optical³ experiments as well as the Hartree-Fock

calculations⁴ 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

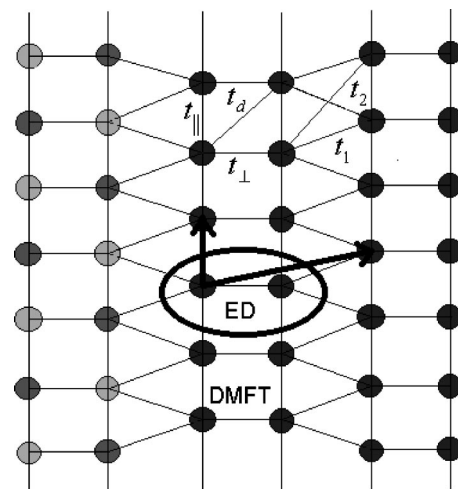


FIG. 1. Schematic representation of the crystal structure of the vanadium layers in NaV_2O_5 and various hopping integrals. The vanadium ions are denoted by filled circles. The ellipse shows the cluster which plays the role of an effective impurity in the dynamical mean-field theory (DMFT) calculations. 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),¹⁴ which can be combined with realistic LDA band-structure calculations (LDA+DMFT).^{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.^{17,18} This extended DMFT scheme has been successfully applied for low-dimensional systems such as two-dimensional high-temperature superconductors^{18,19} and quasi-one-dimensional organic conductors.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_{\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_{\parallel} 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:

$$H = \sum_{ij} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + \sum_i U_i n_{i\uparrow} n_{i\downarrow} + \sum_{i<j,\sigma} V_{ij} n_{i\sigma} n_{j\sigma}, \quad (1)$$

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, $t_1 = 0.012$ eV, $t_2 = 0.03$ eV) was obtained by fitting to the LDA bands.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.²¹ This method applied to NaV_2O_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 *et al.*¹¹ and also by Valenti *et al.*²² for the related LiV_2O_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 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 one d -electron per two V

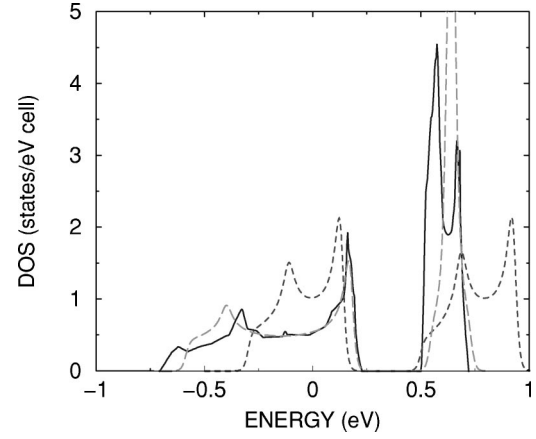


FIG. 2. Bare densities of states (DOS). Solid lines correspond to LDA DOS. The dashed and long-dashed lines represent the first-principles tight-binding parametrizations without and with t_d hopping, respectively.

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_2O_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_{rung} and diagonal interrung V_{diag} parameters $V = V_{rung} - 2V_{diag}$. 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 end 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

$$\mathbf{G}(\mathbf{k}, i\omega) = [(i\omega + \mu) \mathbf{1} - \mathbf{h}(\mathbf{k}) - \mathbf{\Sigma}(i\omega)]^{-1}, \quad (2)$$

where $h_{\alpha\beta}(\mathbf{k})$ is the effective hopping matrix, $\mathbf{\Sigma}_{\alpha\beta}(i\omega)$ is the self-energy matrix of the two-site supercell dimension which is assumed to be local, i.e., \mathbf{k} independent, and μ is the chemical potential.

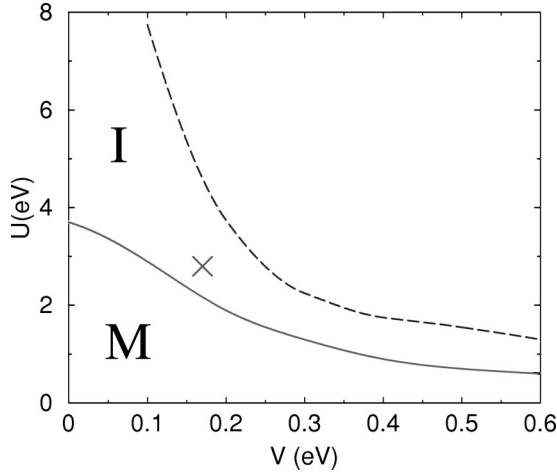


FIG. 3. Calculated phase diagram for the model with the hopping parameter from Ref. 2 (dashed line) and the parameters obtained from our tight-binding-LMTO calculation (solid line). The lines demarcate the metallic and insulating phases in two calculations. The cross corresponds to the lowest bounds values of U and V obtained from our LDA+ U calculation.

In the cluster version of the DMFT scheme,^{17,18} one can write the matrix equation for a bath Green-function matrix \mathcal{G} which describes effective interactions with the rest of the crystal:

$$\mathcal{G}^{-1}(i\omega) = \mathbf{G}^{-1}(i\omega) + \mathbf{\Sigma}(i\omega), \quad (3)$$

where the local cluster Green-function matrix is equal to $G_{\alpha\beta}(i\omega) = \sum_{\mathbf{k}} G_{\alpha\beta}(\mathbf{k}, i\omega)$, 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:

$$\begin{aligned} H_{imp} = & \sum_{i,j,\sigma} T_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + \sum_i U_i n_{i\uparrow} n_{i\downarrow} + \sum_{i<j,\sigma} V_{ij} n_{i\sigma} n_{j\sigma} \\ & + \sum_{k,i,j,\sigma} E_{ij\sigma}(k) a_{ki\sigma}^{\dagger} a_{kj\sigma} \\ & + \sum_{k,i,j,\sigma} \Gamma_{ij\sigma}(k) (a_{ki\sigma}^{\dagger} c_{j\sigma} + \text{H.c.}), \end{aligned} \quad (4)$$

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 $k=1, \dots, n_b$, respectively.

For the iterative solution of the effective impurity model Eq. (4) we use the Lanczos version of the ED method.¹⁴ The orbital energy matrix for the conduction band $E_{ij\sigma}(k)$, and the corresponding hybridization elements $\Gamma_{ij\sigma}(k)$, are the effective parameters which reproduce the bath Green function:

$$\mathcal{G}^{-1}(i\omega_n) = (i\omega_n + \mu) * \mathbf{1} - \mathbf{T} - \sum_k \mathbf{\Gamma}_k [i\omega_n - \mathbf{E}_k]^{-1} \mathbf{\Gamma}_k^{\dagger}.$$

In the paramagnetic case we can transform \mathcal{G} , \mathbf{T} , $\mathbf{\Gamma}_k$, and \mathbf{E}_k matrices of the dimension 2×2 for our cluster to the diago-

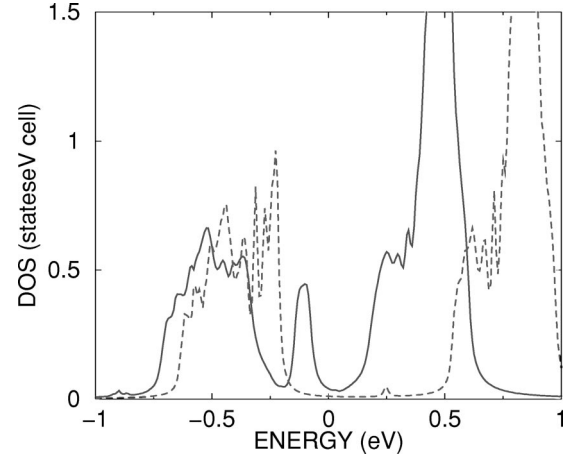


FIG. 4. The renormalized densities of states (only the lower Hubbard bands) obtained in our DMFT calculation with parameters $U=2.8$ eV and $V=0.17$ eV (solid line), and $U=2.8$ eV and $V=0.5$ eV (dashed line).

nal *bonding-antibonding* basis $\lambda = \{b, a\}$. In this case $T_{\lambda} = \{-t_{\perp}, t_{\perp}\}$ and $\mathcal{G}_{\lambda} = \{\mathcal{G}_b, \mathcal{G}_a\}$, where $\mathcal{G}_{b,a} = \mathcal{G}_{11} \pm \mathcal{G}_{12}$. We used ten bath orbitals for our two-site cluster.

The parameters $\{E_{k\lambda\sigma}, \Gamma_{k\lambda\sigma}\}$ are now fitted to reproduce the bath Green function $\mathcal{G}_{\lambda\sigma}(i\omega_{\nu})$ 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 $\mathbf{\Sigma}_{ij\sigma}(i\omega_{\nu})$ which are required for the next DMFT iterations. After solving the effective cluster problem using the Lanczos algorithm, the local Green's-function matrix $G_{ij\sigma}(i\omega_{\nu})$ was determined and the cluster self-energy $\mathbf{\Sigma}_{ij\sigma}(i\omega_{\nu})$ 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.²³ 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 NaV₂O₅.²⁴ 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 experiment³) 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. The

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 NaV_2O_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 NaV_2O_5 have also appreciable weight.

We conclude that the insulating state of NaV_2O_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 NaV_2O_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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