

Charge Ordering and Spin Gap in NaV_2O_5

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A possible ground state of NaV_2O_5 is proposed based on the Hartree approximation for both on-site and intersite Coulomb interactions. The results indicate that the intersite Coulomb interaction induces a zigzag type of charge disproportionation (i.e. charge ordering) along the ladders of V-ions resulting in the localized spins between neighboring ladders to form a spin gap. This new state, which is different from the spin-Peierls state so far believed, seems to be consistent with the existing experimental results.

KEYWORDS: NaV_2O_5 , spin gap, charge ordering, Hartree approximation, spin-Peierls, charge disproportionation

Recently NaV_2O_5 has been attracting interest.¹⁾ Based on early structural study which postulated two different V sites, i.e. V^{4+} -ions and nonmagnetic V^{5+} -ions,²⁾ this compound has been considered to be described by a simple spin 1/2 Heisenberg chain consisting of V^{4+} resulting in the spin-Peierls (SP) state.

However, there are many controversial issues as regards the nature of this material. The X-ray superlattice reflection below the transition temperature $T_c = 35$ K where the magnetic susceptibility steeply decreases, shows that the unit cell gets four times larger along the c -axis (the chains are along the b -axis), which is not expected from simple SP dimerized lattice distortion.³⁾ On the other hand, in an inelastic neutron scattering measurement below T_c , two excitation branches along the a^* -axis together with an intensity modulation were observed along the a^* -axis, which can not be explained based on simple 1D SP chains.⁴⁾ Furthermore, a recent crystal structural analysis showed that the V-ions are all equivalent at room temperature thus have valences $4.5+$,^{5,6)} while a ^{51}V -NMR experiment on single-crystalline sample of NaV_2O_5 revealed that these V sites change its valences at T_c from uniform $\text{V}^{4.5+}$ to two different sites of V^{4+} and V^{5+} .⁷⁾ At the same time, Δ/T_c , where Δ is the spin gap energy, is significantly large compared to other SP compounds, e.g. TTF-CuBDT, MEM-(TCNQ)₂ and CuGeO_3 .³⁾

The causes of these puzzling experimental results is poorly understood, and even the origin of the observed insulating behavior in the whole temperature range is not clear yet. As regards the orbitals of d -electrons at V sites, those with d_{xy} symmetry are suggested to be relevant above and below T_c ,^{8,5)} and then this d_{xy} -band is nominally 1/4-filled. There are theoretical studies based on the assumption of charge ordering into chains of V^{4+} and V^{5+} on one hand,^{9,10)} while there is a proposal that each electron is located in a bonding V-O-V molecular wavefunction.^{5,11)} However, as has been clarified in charge-transfer organic compounds,^{12,13)} there exist var-

ious possibilities of charge distribution in 1/4-filled systems triggered by the intersite Coulomb interaction when the geometry and consequently transfer integrals of the system are very anisotropic.

In this letter, the possibility of a charge ordering in the ground state of NaV_2O_5 has been pursued by use of the Hartree calculations including intersite Coulomb interaction. Furthermore, the origin of the spin gap behavior is discussed based on these results.

To investigate the effect of Coulomb interaction, the V_2O_5 layer, namely its a - b plane is considered, where the spatial arrangement of V-ions is schematically shown in Fig. 1. They form two-leg ladders in the b -direction and these ladders align in the a -direction; a unit cell contains four vanadiums as in Fig. 1. The hopping parameters between them, t_a, t_b, t_{xy} , the on-site and the intersite Coulomb interactions, U and $V_{i,j}$, respectively, are taken into account; we define $V_{i,j} = V_a, V_b, V_{xy}$ as the interaction along the bond with hopping t_a, t_b, t_{xy} , respectively, as in Fig. 1. Our Hamiltonian is a model of single orbital, d_{xy} , for each vanadium site given as follows;

$$H = \sum_{\langle i,j \rangle} \sum_{\sigma} \left(-t_{i,j} a_{i\sigma}^{\dagger} a_{j\sigma} + h.c. \right) + \sum_i U n_{i\uparrow} n_{i\downarrow} + \sum_{\langle i,j \rangle} V_{i,j} n_i n_j, \quad (1)$$

where $\langle i, j \rangle$ denotes the neighbor site pair, σ is a spin index which takes \uparrow and \downarrow , $n_{i\sigma}$ and $a_{i\sigma}^{\dagger}$ ($a_{i\sigma}$) denote the number operator and the creation (annihilation) operator for the electron of spin σ at the i th site, respectively, and $n_i = n_{i\uparrow} + n_{i\downarrow}$.

The Coulomb interactions U , $V_{i,j}$ are treated within the Hartree approximation in a manner similar to that in refs. 12 and 13,

$$n_{i\uparrow} n_{i\downarrow} \rightarrow \langle n_{i\uparrow} \rangle n_{i\downarrow} + n_{i\uparrow} \langle n_{i\downarrow} \rangle - \langle n_{i\uparrow} \rangle \langle n_{i\downarrow} \rangle$$

$$n_i n_j \rightarrow \langle n_i \rangle n_j + n_i \langle n_j \rangle - \langle n_i \rangle \langle n_j \rangle, \quad (2)$$

and self-consistent solutions are searched for. Our calculations are carried out at $T = 0$ and the average electron

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density is fixed at 1/4 per vanadium site. Several types of antiferromagnetic (AF) solutions are obtained and their energies are compared so that the true ground state is determined. The total energy \mathcal{E} is calculated as

$$\mathcal{E} = \frac{1}{N_{cell}} \sum_{lk\sigma} \epsilon_{lk\sigma} n_F(\epsilon_{lk\sigma}) - \sum_i U \langle n_{i\uparrow} \rangle \langle n_{i\downarrow} \rangle - \sum_{\langle i,j \rangle} V_{i,j} \langle n_i \rangle \langle n_j \rangle, \quad (3)$$

where N_{cell} is the total number of the cells, $\epsilon_{lk\sigma}$ is the l th eigenvalue at each k and $n_F(\epsilon)$ is the Fermi distribution function.

The AF solutions we found to be stable are shown in Fig. 2. The ‘dimer’ type AF (Fig. 2(a)) has uniform charge density, i.e. 0.5 electron per site, and, if the pairs of vanadium are taken as dimers, it can be considered as AF between these dimers along the ladders, which corresponds to the state assumed in refs. 5 and 11. In the ‘chain’ type AF (Fig. 2(b)), charge disproportionation (charge ordering) exists; the charges concentrate on one leg of the ladders, and AF ordering emerges along these chains. This type corresponds to the conventional 1D V^{4+} spin 1/2 chains. The ‘zigzag’ type AF is the one newly found, which also has the charge disproportionation but the sites with more electrons, i.e. V^{4+} , are distributed in a zigzag way along the ladders as in Fig. 2(c). In the actual solutions obtained by Hartree calculations, there exist, to be precise, finite but small spin moments on the sites which are described as open circles. However, as we will see below, within realistic range of parameters, these spin moments are small so that they can be neglected.

For the explicit calculations the values of parameters are taken from ref. 11 as $t_a = 0.35$ eV, $t_b = 0.15$ eV, $t_{xy} = 0.3$ eV and $U = 4.0$ eV, and $V_{i,j}$ are varied maintaining the condition $V \equiv V_a = V_b = V_{xy}/\sqrt{2}$. Here we assumed $V_{i,j} \propto 1/d_{i,j}$, where $d_{i,j}$ is the distance between the $\langle i, j \rangle$ pair, and approximated that the distances between intraladder vanadiums are all same and the distance of interladder vanadiums is $\sqrt{2}$ times smaller than that. The calculated energies of each state as a function of V for three different types of AF solutions together with that for the paramagnetic solution are shown in Fig. 3. This result shows that ‘zigzag’ type of AF has the lowest energy within a range of realistic values of V , namely $V \sim 1$ eV. The magnitudes of spin moment on sites 1 and 2 (see the inset of Fig. 4 where a unit magnetic cell is shown), $S_z(i)$ ($i=1,2$), and the amount of charge disproportionation δ in this case of ‘zigzag’ type AF are shown in Fig. 4. We note that the charge densities are $0.5+\delta$ on sites 1 and 4, $0.5-\delta$ on sites 2 and 3, and the spin moments have the relation $S_z(1)=-S_z(4)$ and $S_z(2)=-S_z(3)$. When V is decreased, this ‘zigzag’ state gives away continuously to the ‘dimer’ state at $V = V_c$, where $S_z(1)=S_z(2)=-S_z(3)=-S_z(4)$. When $V \gtrsim 0.5$ eV, which is expected to be realistic, $\delta \simeq 0.5$, i.e. the charge is almost concentrated in sites 1 and 4, and $|S_z(1)|=|S_z(4)| \simeq 1.0$ ($|S_z(2)|=|S_z(3)| \simeq 0$). Hence we can consider that the electrons are almost fully localized on sites 1 and 4 to form V^{4+} while V^{5+} in sites 2 and 3.

If quantum fluctuation is taken into account in this state where localized 1/2 spins exist on the sites 1 and 4, it is easy to imagine that the pairs of nearest spins, which is along the bond with hopping t_{xy} , form essentially a localized singlet.

There exists a different proposal for the values of the hopping integrals with very small t_{xy} , i.e. $t_a = 0.38$ eV, $t_b = 0.17$ eV and $t_{xy} \ll 0.1$ eV.⁵⁾ We note, however, the result of our Hartree calculations even for $t_{xy} = 0$ eV does not show qualitative difference from those given in Figs. 3 and 4. We also note that the results are not largely affected by the condition $V_a = V_b = V_{xy}/\sqrt{2}$ that we adopted; the results for $V_a = V_b = V_{xy}$ show the same features.

Now we compare our present results of the ground state with the ‘zigzag’ pattern of charge ordering, and the various experimental results noted above. The spin gap behavior in the magnetic susceptibility measurement¹⁾ can be understood as the spin singlet formation as discussed above. This is not a SP state and then the comparison of Δ/T_c ³⁾ to other SP compounds is irrelevant. The change in valences through T_c observed in the NMR measurement⁷⁾ may be due to the phase transition from the ‘dimer’ state above T_c to the ‘zigzag’ state below T_c . The ‘zigzag’ type charge ordering result in the period of two V sites in the b -direction and of four ladders in the a -direction (see Fig. 2(c)), namely doubles the original unit cell size in the a - b plane, which is consistent with the observed results below T_c .³⁾ The excitation spectra from the ‘zigzag’ singlet ground state is an unanswered question, but a deviation from 1D character is expected. Thus it is natural that the inelastic neutron scattering measurement showed a dispersion which is not expected from 1D SP chains.⁴⁾ However, more experimental studies, especially the firm determination of crystal structure both below and above T_c are needed for further discussions, e.g. regarding the unit cell size enlargement along the c -direction³⁾ and the intensity modulation along the a^* -axis in the inelastic neutron scattering measurement.^{4,14)}

In summary, the ground state of NaV_2O_5 is investigated within the Hartree approximation for both on-site and intersite Coulomb interactions. The effect of intersite Coulomb interaction results in a zigzag pattern of V^{4+} along the ladders of vanadiums resulting in the singlet pairs, which is different from the conventional picture that this compound is a spin-Peierls system. This proposed ground state is consistent with the observed spin gap and also with the other experimental results so far reported.

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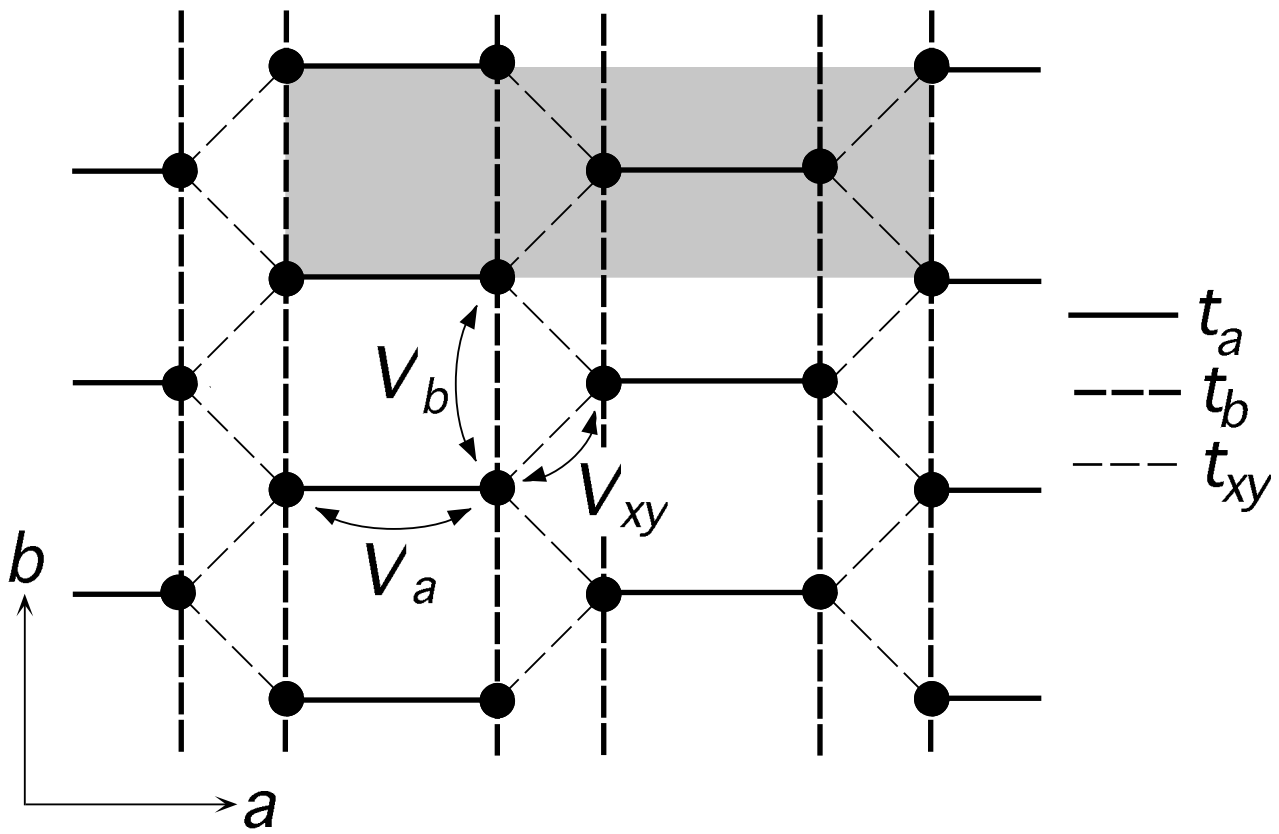
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- [14] In ref. 4, it is discussed that this unexpected intensity modulation can be explained if the positions of the V^{4+} and V^{5+} chains alternate from one layer to another. Similarly, the alternation of the pattern of charge ordering in the c -direction in the presence of the ‘zigzag’ pattern may explain this modulation.

Fig. 1. A schematic representation of the structure of V ions in the a - b plane of NaV_2O_5 , where V ions are represented as black circles, together with the hopping integrals (after the notations of ref. 11), and the intersite Coulomb interactions $V_{i,j}$. Thick, thick-dotted, and thin-dotted lines representing the hopping parameters t_a , t_b and t_{xy} , respectively.

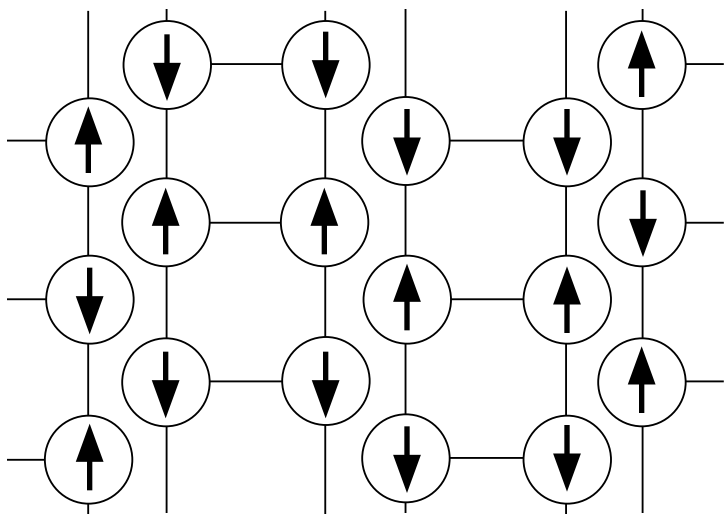
Fig. 2. A schematic view of different types of AF ordering for the structure given in Fig. 1. Circles and arrows represent V-ions and the spin moments, and $+\delta$ and $-\delta$ denote the amount of charge disproportionation (charge ordering) $0.5+\delta$ and $0.5-\delta$, namely more or less electrons than the average, respectively.

Fig. 3. The energy per unit magnetic cell of each state shown in Fig. 2. The inset shows the region of small V .

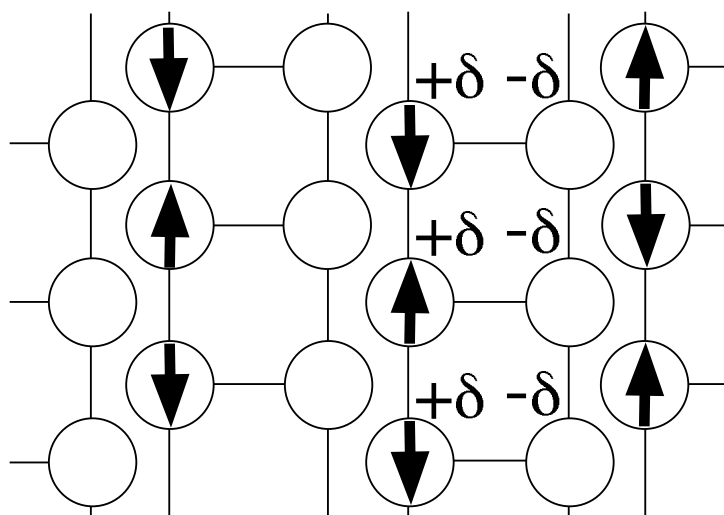
Fig. 4. The spin moment, S_z , and the degree of charge disproportionation, δ , for the zigzag type AF as a function of V . The inset shows the magnetic unit cell along the ladder with the site indices, where the alignment of the spin moments are indicated by arrows and the amount of charge is $0.5+\delta$ and $0.5-\delta$, respectively.



(a) 'dimer'



(b) 'chain'



(c) 'zigzag'

