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# Charge ordering and opening of spin gap in $\text{NaV}_2\text{O}_5$

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## Abstract

We argue that the origin of the phase transition in quasi-one-dimensional antiferromagnet  $\text{NaV}_2\text{O}_5$  is not the spin-Peierls (SP) instability, but a charge ordering. The opening of the spin gap and the lattice dimerization, characteristic for the spin-Peierls systems, in  $\text{NaV}_2\text{O}_5$  result from the interplay between the charge, lattice, and spin degrees of freedom. © 1999 Elsevier Science Ltd. All rights reserved.

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Quasi-one-dimensional antiferromagnets, such as TTF-CuBDT,  $\text{MEM}(\text{TCNQ})_2$ ,  $\text{CuGeO}_3$ , undergo the spin-Peierls (SP) transition into a state, in which neighboring spins form singlet pairs, the chain lattice is dimerized and the spectrum of the magnetic excitations has a gap. The driving force of this transition is the instability of the quasi-one-dimensional spin system against the singlet formation. The specific features of the SP systems are the strong dependence of the transition temperature on magnetic field and the transition into the incommensurate state at high magnetic field [1,2].

It can also turn out, however, that the spin-gap opening, rather than being responsible for the lattice deformation, is, in fact, its consequence, while the deformation occurs because of some other instability. In this case the thermodynamics would be quite different from that of SP systems, since spins and phonons are not the only low-energy degrees of freedom [1]. In this paper we argue that the recently discovered inorganic compound  $\text{NaV}_2\text{O}_5$  is an example of such a pseudo-spin-Peierls system and that the phase transition observed in this material is mainly related to a charge ordering, which occurs in many oxides and is actively studied now in the context of colossal magnetoresistance and high- $T_c$  materials.

Initially  $\text{NaV}_2\text{O}_5$  was identified as an inorganic SP material similar to  $\text{CuGeO}_3$ . According to the early X-ray studies [3],  $\text{V}^{4+}$  ions form spin-1/2 chains separated by non-magnetic  $\text{V}^{5+}$ -chains. Magnetic susceptibility, X-ray and

neutron scattering data show the opening of the spin gap below  $T_c = 34$  K and the doubling of the lattice period in the chain direction [4–6].

However, according to the new X-ray and neutron data [7–9], at room temperature all V sites are equivalent ( $\text{V}^{4.5+}$ ). Other indications that the physics of  $\text{NaV}_2\text{O}_5$  is different from that of, e.g.  $\text{CuGeO}_3$  come from thermodynamic data. Thus the study of specific heat shows that the entropy of the transition in  $\text{NaV}_2\text{O}_5$  is larger than the entropy of a pure SP system [10] (also B. Büchner, private communication). The ratio  $(2\Delta_0/T_c)$ , where  $\Delta_0$  is the value of the spin gap, is for  $\text{NaV}_2\text{O}_5 \sim 6$  [5], while for all known SP materials it is close to 3.5 [1]. Another evidence against the interpretation of the phase transition in  $\text{NaV}_2\text{O}_5$  as a SP transition is a very weak dependence of  $T_c$  on magnetic field: the shift of  $T_c$  is  $\sim 5$  times smaller [10] than the theoretical predictions [1,2]. The temperature-dependence of the thermal conductivity of  $\text{NaV}_2\text{O}_5$  is also remarkably different from that of  $\text{CuGeO}_3$  [11].

All these facts show that the phase transition in  $\text{NaV}_2\text{O}_5$  is not an ordinary SP transition. We suggest that the main phenomenon responsible for the transition is a charge ordering (CO): while in the high-temperature phase the fast exchange between  $\text{V}^{4+}$  and  $\text{V}^{5+}$  makes all V sites equivalent, in the low-temperature phase there are two kinds of V ions with different charges. The appearance below  $T_c$  of two inequivalent V sites was indeed observed in the recent NMR experiment [12]. We show here that the opening of a spin gap is just one of the consequences of this CO.

The structure of  $\text{NaV}_2\text{O}_5$  consists of  $\text{V}_2\text{O}_5$  layers with

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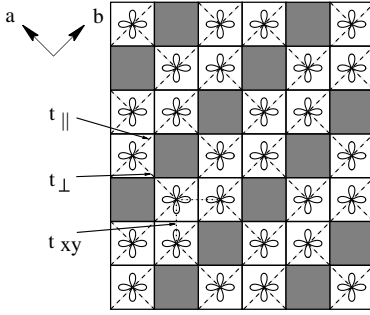


Fig. 1. The crystal structure of V–O plane of  $\text{NaV}_2\text{O}_5$ : oxygens are located at the corners of plaquettes, while V ions are located at their centers; the shaded plaquettes are vacant. Also shown are the relevant  $d_{xy}$ -orbitals of V ions and V ladders (dashed lines).

approximately square oxygen lattice and V ions located in the middle of two out of every three oxygen plaquettes (see Fig. 1). Due to special orbital structure the diagonal (next-nearest-neighbor (nnn)) hopping amplitudes,  $t_{\perp}$  and  $t_{\parallel}$ , are much larger than the nearest-neighbor (nn) hopping amplitude  $t_{xy}$  ( $t_{\perp} \sim 0.38$  eV,  $t_{\parallel} \sim 0.17$  eV, and  $t_{xy} \sim 0.012$  eV [7]). Thus,  $\text{NaV}_2\text{O}_5$  is a system of V two-leg ladders with one electron per rung occupying a bonding state with the energy  $-t_{\perp}$ . For strong on-site Coulomb repulsion the energy cost of electron transfer on a neighboring rung is  $\geq 2t_{\perp}$ , so that for  $2t_{\perp} > 4t_{\parallel}$  the system is insulating and can be described as a system of spins localized on the rungs of V ladders [7,13].

In this paper we take into account also the charge dynamics in  $\text{NaV}_2\text{O}_5$ . We start from the electronic Hamiltonian, which includes the electron hopping in and between ladders (see Fig. 1), as well as the Coulomb interaction between electrons on different V sites: the nn interaction  $V_2$  (e.g. between sites C and D on neighboring ladders in Fig. 3), the nnn interaction  $V_1$  inside ladders (e.g. between sites A and E or B and E in Fig. 3), etc. The on-site Coulomb repulsion  $U$  is the largest parameter and is here taken as infinite.

Next we make a projection on the subspace of states with one electron per rung. Four different states of a single electron on a rung can be represented as the eigenstates of spin  $S = 1/2$  and isospin  $T = 1/2$  operators,  $|1/2, S^z\rangle \otimes |1/2, T^z\rangle$ , where  $T^z = \pm 1/2$  corresponds to an upper/lower position of the electron on a rung (see Fig. 3).

The effective spin–isospin Hamiltonian can then be written in the form  $H = H_0 + H_1$ , where  $H_0$  is a pure isospin Hamiltonian:

$$H_0 = -2t_{\perp} \sum_{\mathbf{r}} T_{\mathbf{r}}^x + 2V_1 \sum_{\mathbf{r}} \left( T_{\mathbf{r}}^z T_{\mathbf{r}+\mathbf{b}}^z + \frac{1}{4} \right) + 2V_2 \sum_{(\mathbf{r}_1, \mathbf{r}_2)} \left( \frac{1}{4} - T_{\mathbf{r}_1}^z T_{\mathbf{r}_2}^z \right) + H'_0. \quad (1)$$

Here, the vector  $\mathbf{r}$  runs over the rungs of V ladders. The first

term in Eq. (1) describes the electron hopping in the rungs, the second term is the nnn Coulomb interaction between electrons occupying neighboring rungs  $\mathbf{r}$  and  $\mathbf{r} + \mathbf{b}$  of a ladder, the third term is the repulsion between nn electrons from neighboring ladders, and  $H'_0$  denotes all other interaction terms (the longer range Coulomb terms, the interaction via the lattice, etc.).

The Hamiltonian  $H_1$  describes the spin–isospin interaction. The strongest interaction occurs inside ladders. For  $t_{\parallel} \ll t_{\perp}$ ,  $V_1$ , the corresponding Hamiltonian of a single ladder has the form:

$$H_1 = -\frac{4t_{\parallel}^2}{\Delta} \sum_n \left[ \left( \frac{1}{4} - \mathbf{S}_n \cdot \mathbf{S}_{n+1} \right) \left( \frac{1}{4} + \mathbf{T}_n \cdot \mathbf{T}_{n+1} - 2T_n^z T_{n+1}^z \right) + \left( \frac{3}{4} + \mathbf{S}_n \cdot \mathbf{S}_{n+1} \right) \left( \frac{1}{4} - \mathbf{T}_n \cdot \mathbf{T}_{n+1} \right) \right], \quad (2)$$

where  $n$  runs over the rungs of the ladder. The Hamiltonian (2) resembles the effective spin–isospin interaction for the Hubbard model with two degenerate orbitals [14,15]. It results from the virtual electron hopping on neighboring rungs,  $\Delta$  being the energy difference between the virtual and the ground states. The value of  $\Delta$  is determined by  $H_0$  and depends on a state considered. If, e.g. we neglect the Coulomb terms in the disordered phase, then  $\Delta = 2t_{\perp}$ , while for the extreme zigzag CO discussed below:  $\Delta \sim 2V_1$ . Note, that in the  $U \rightarrow \infty$  limit  $\Delta$  is finite.

The spin–isospin structure of the exchange interaction  $H_1$  follows from the Pauli principle: the wave function of two neighboring electrons in the intermediate state (when they occupy the same rung) is antisymmetric under the exchange of both their spin and isospin coordinates. Therefore, if the spin state of two electrons on neighboring sites  $n$  and  $n+1$  is antisymmetric (the total spin,  $\mathbf{S} = \mathbf{S}_n + \mathbf{S}_{n+1}$ , is 0), their isospin state has to be symmetric (the total isospin  $\mathbf{T} = \mathbf{T}_n + \mathbf{T}_{n+1}$  has to be 1) and, vice versa, if  $S = 1$ , then  $T = 0$ . Correspondingly, the first term in square brackets of Eq. (2) is the projection operator on  $S = 0$ ,  $T = 1$ ,  $T^z = 0$  state, while the second term is the projection operator on  $S = 1$ ,  $T = 0$  state. The projection of the total isospin of two electrons,  $T^z$ , in both terms is zero, because for infinitely large on-site Coulomb repulsion  $U$  the hopping between rungs is only possible if electrons are located on different chains of the ladder.

Since  $H_1$ , obtained by the second-order perturbation in the interrung hopping, is smaller than  $H_0$ , we can start by considering only the charge degrees of freedom. The isospin Hamiltonian  $H_0$  describes the competition between the hopping in the rungs, which tends to make V ions equivalent, and the Coulomb interaction, which favors a CO. If, e.g. we leave only the first two terms in Eq. (1), the ladders become decoupled and the Hamiltonian of each ladder is the Hamiltonian of the Ising model in perpendicular magnetic field. For  $V_1 < 2t_{\perp}$  its ground state is disordered (all V ions are equivalent), while in the opposite case, isospins in the

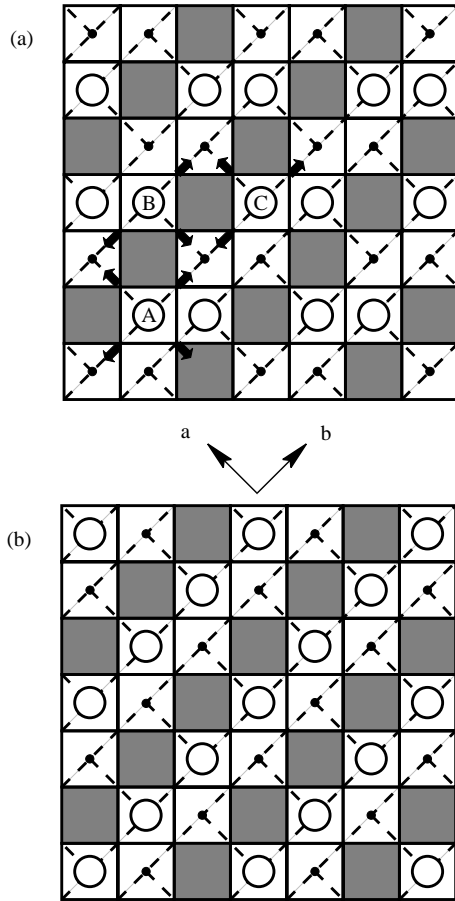


Fig. 2. Two types of CO: the zigzag structure (a) and the old structure, in which  $V^{4+}$  chains are separated by  $V^{5+}$  chains (b). Large circles denote  $V^{4+}$  ions with the large ionic radius, while small circles denote small nonmagnetic  $V^{5+}$  ions. Arrows show shifts of oxygen atoms around  $V^{4+}$  ions in one ladder (for simplicity, the shifts induced by  $V^{4+}$  ions in other ladders are not shown).

ground state are ordered antiferromagnetically:  $\langle 2T_n^z \rangle = \eta(-1)^n$ . This CO corresponds to the zigzag occupation of vanadium sites by electrons, like the one shown in Fig. 2a, where the large circles denote  $V^{4+}$  ions with the large ionic radius and the small circles denote small nonmagnetic  $V^{5+}$  ions.

On the other hand, the third term in Eq. (1) favors the structure shown in Fig. 2b, which would give the spin chains of  $V^{4+}$  ( $d^1, S = 1/2$ ) ions and is the initially assumed crystal structure [3]. If we would take into account only the second and the third terms with  $V_2 = \sqrt{2}V_1$ , the zigzag structure (Fig. 2a) would have lower energy than the chain structure (Fig. 2b). For real long-range Coulomb interaction, the Madelung energies of these structures appear to be rather close, the chain structure of Fig. 2b being slightly more favorable.

There is, however, another type of interaction between

charges—the interaction via lattice distortions. As shown in Fig. 2a, this latter interaction definitely favors the zigzag structure: large  $V^{4+}$  ions push out neighboring oxygens (the directions of oxygen displacements in a ladder are shown in Fig. 2a by arrows). As a result, neighboring plaquettes in a ladder would preferably be occupied by smaller  $V^{5+}$  ions.

Note, that the zigzag structure shown in Fig. 2a immediately gives the doubling of the lattice period in both  $a$  and  $b$  directions observed in the experiment [5]. Thus, one does not need to invoke the SP mechanism to explain the distortion pattern below  $T_c$ . We also note, that there exist four equivalent realizations of the zigzag structure of Fig. 2a, which differ by the location and orientation of pairs of nn  $V^{4+}$  ions (large circles in Fig. 2a). This may provide a clue to understanding of the four-fold increase of the period in  $c$ -direction below  $T_c$  [5].

The isospin excitation corresponds to an electronic transition from the symmetric state on a rung ( $T^x = +1/2$ ) to the antisymmetric one ( $T^x = -1/2$ ). Due to Coulomb interactions these on-rung excitons can hop on other rungs and thus form a band. For a general form of the interrung Coulomb interactions,  $\sum_{r,r'} V_{r,r'} T_r^z T_{r'}^z$ , the exciton dispersion above  $T_c$ , obtained in the random phase approximation, is given by

$$E_{\mathbf{q}} = \sqrt{2t_{\perp}(2t_{\perp} + \langle T^x \rangle V(\mathbf{q}))}, \quad (3)$$

where  $V(\mathbf{q})$  is a Fourier transform of  $V_{r,r'}$  and  $\langle T^x \rangle = (1/2) \tanh(t_{\perp}/T)$  is the average value of  $T_i^x$ . The strong peak at  $\sim 1$  eV in the optical absorption spectrum for electric field applied in  $a$ -direction [16] can then be related to the  $\mathbf{q} = 0$  isospin excitation.

The excitonic gap  $\Delta = E_{\mathbf{q}_0}$ , where  $\mathbf{q}_0$  is the wave vector at which  $V(\mathbf{q})$  has minimum, may, however, be much smaller than 1 eV, as  $|V(\mathbf{q})|$  is of the same order as  $2t_{\perp}$ . The continuum of several soft isospin excitations may explain the broad peak at  $\sim 0.1$  eV observed in Ref. [16]. In our scenario we assume that  $\mathbf{q}_0 = (1/2, 1/2, 1/4)$ ,  $V(\mathbf{q}_0) < 0$  and that the isospin excitations soften at  $T = T_c$ , i.e. the gap  $\Delta$  vanishes at transition temperature. The mean field expression for  $T_c$  is:

$$\tanh \frac{t_{\perp}}{T_c} = \frac{4t_{\perp}}{|V(\mathbf{q}_0)|}. \quad (4)$$

As  $T_c \ll t_{\perp}$ , the charge system should be close to the quantum critical point, at which the transition between the ordered and disordered state occurs at zero temperature. The soft isospin excitations can be directly observed by measuring the electron energy loss spectrum at low energy.

Below  $T_c$  the nonzero  $\langle T_r^z \rangle = M^z \cos(\mathbf{q}_0 \mathbf{r} + \phi)$  appears, corresponding to the zigzag CO. Since the coupling to electric field parallel to  $a$ -axis in our model has the form,  $-\alpha E_a \sum_r T_r^z$  and the zigzag ordering corresponds to “antiferromagnetic” ordering of isospins, the temperature dependence of the dielectric constant  $\epsilon_a$  close to  $T_c$  should be similar to that of the parallel magnetic susceptibility of an

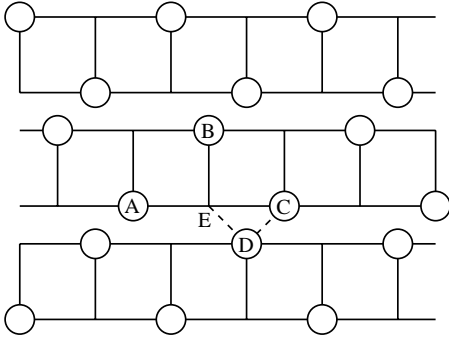


Fig. 3. This figure demonstrates that the zigzag CO makes the spin-exchange in neighboring pairs of electrons (AB and BC) inequivalent. The inequivalence is caused by the difference in the occupation of V sites in neighboring ladders.

antiferromagnet. Such behavior was indeed observed experimentally [17,18].

Next we consider the spin excitations. From Eq. (2) the effective spin-exchange constant in the ladder direction,  $J_{\parallel}$ , is:

$$J_{\parallel} = \frac{4t_{\parallel}^2}{\Delta} \langle \mathbf{T}_n \cdot \mathbf{T}_{n+1} - T_n^z T_{n+1}^z \rangle = \frac{4t_{\parallel}^2}{\Delta} \langle T_n^x T_{n+1}^x + T_n^y T_{n+1}^y \rangle, \quad (5)$$

where  $\langle \dots \rangle$  denotes the thermal and quantum average. From Eq. (5) it follows that CO results in the decrease of the spin-exchange constant below  $T_c$ . In particular, if the electrons on neighboring rungs are completely uncorrelated, then  $\langle T_n^x T_{n+1}^x + T_n^y T_{n+1}^y \rangle = 1/2$ , while for the extreme zigzag CO ( $\eta = 1$ )  $\langle \mathbf{T}_n \cdot \mathbf{T}_{n+1} \rangle = \langle T_n^z T_{n+1}^z \rangle$ , and  $J_{\parallel} = 0$ . In general, the charge order parameter  $\eta < 1$ , so that the CO results only in a partial reduction of  $J_{\parallel}$ . The decrease with temperature of the spin stiffness in  $b$ -direction could be observed in neutron scattering experiments.

More importantly, the zigzag CO can open a spin gap. There are, in principle, two scenarios for the spin-gap opening. First, as one can see from Fig. 2a, the CO results in the appearance of pairs of nn vanadiums coupled by the hopping amplitude  $t_{xy}$ , (cf. Fig. 1). For large  $t_{xy}$  these interladder pairs would form spin singlets, which could explain the spin gap in  $\text{NaV}_2\text{O}_5$ . However, we think that this is rather unlikely. On the one hand, as we mentioned above, the band structure calculations give rather small value of  $t_{xy}$  [7]. On the other hand, even for larger  $t_{xy}$  (as, e.g. in Ref. [13]) there are several competing mechanisms of nn exchange: an antiferromagnetic one due to direct d–d overlap, and an exchange via  $90^\circ$  V–O–V path, which is ferromagnetic. Even the sign of the resulting interaction is unclear: in Ref. [13] a small antiferromagnetic nn exchange was obtained, while the LDA + U calculations for the structurally similar material  $\text{CaV}_2\text{O}_5$  give a ferromagnetic nn interaction [19]. Furthermore, in  $\text{NaV}_2\text{O}_5$  there is a third mechanism of exchange resulting from the circular motion of electrons over V

triangles (e.g. along the CDE triangle in Fig. 3). The sign of the latter exchange coincides with the sign of the product of three amplitudes of electron hopping along the sides of a triangle (cf. Ref. [20]). As the latter sign is negative [7], the corresponding exchange is ferromagnetic.

Thus, whether the interladder singlets are formed or not, is still not clear. It is, however, obvious that the zigzag CO results in an alternation of the exchange constants along the spin chains formed by V ladders. Indeed, the exchange interaction between the ions A and B (see Fig. 3) goes via a plaquette having  $V^{5+}$  both above and below it, whereas for B and C ions the corresponding positions are occupied by  $V^{4+}$  ions. This inequivalence in the occupation of V sites in neighboring ladders results in the alternation of the exchange constants along the ladder direction,  $J_{\parallel}(n, n+1) = J_{\parallel}(1 + (-1)^n \delta)$ , which opens the spin gap.

Although the opening of the spin gap is not the main driving force of the transition, it may be important for determining the relative phases of charge order parameter  $\eta$  in different ladders. If, e.g.  $\eta$  in the bottom ladder in Fig. 3 would have opposite sign, there would be no doubling of the periodicity in  $a$ -direction and no alternation in the spin-exchange constants along the ladders, and consequently, no spin gap. The energy gain due to the spin-gap opening, by itself, can make the structure of Fig. 2a more stable than the zigzag structure without the dimerization along  $a$ -axis.

Summarizing, we argued that  $\text{NaV}_2\text{O}_5$  is not a SP material, but a new low-dimensional system with charge ordering, in which magnetic  $V^{4+}$  sites form zigzags in the V ladders. We argued, that this charge ordering results in the doubling of the lattice period both in  $a$ - and  $b$ -directions and may also explain the appearance of a period 4 in  $c$ -direction, as well as the anomalous behavior of the dielectric constant. Another consequence of this charge ordering is the alternation of the exchange interaction along V ladders, which opens the spin gap. This picture is consistent with the main experimental observations for  $\text{NaV}_2\text{O}_5$ . Our consideration shows that one has to be careful in ascribing the origin of the spin gap to the spin system itself: it may be a consequence of some other effects, here—zigzag charge ordering in quarter-filled ladders.

After completion of this work two papers appeared [21,22] in which similar ideas were put forward. Thalmeier and Fulde [22] argued in favor of the CO shown in Fig. 2b, after which they still had to invoke the spin–lattice coupling to get second transition of a SP type. In their model the largest electron hopping amplitude  $t_{\perp}$  was completely neglected, which would result in the random exchange between electron spins above  $T_c$ , instead of the quasi-one-dimensional behavior. Also, the recent careful study [10] did not confirm the presence of the second transition in  $\text{NaV}_2\text{O}_5$ . The picture of Seo and Fukuyama [21] is closer to ours: they also concluded that the zigzag structure is more favorable. Their arguments, however, are based on nn and nnn Coulomb terms only, which is definitely insufficient (as we mentioned above, the long range Coulomb interaction

by itself would favor the structure of Fig. 2b). Furthermore, their singlets are formed by nn pairs between ladders, which, as we argued above, is rather unlikely.

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