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LETTER TO THE EDITOR

On the stacking charge order in NaV_2O_5

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Abstract

We propose a mechanism for the observed stacking charge order in the quarter-filled ladder compound NaV_2O_5. Via a standard mapping of the charge degrees of freedom onto Ising spins we explain the stacking order as a result of competition between couplings of the nearest and next-nearest planes with the four-fold degenerate super-antiferroelectric in-plane order.

(Some figures in this article are in colour only in the electronic version)

There has been a great interest in recent years from both theorists and experimentalists in the insulating transition-metal compound NaV_2O_5 [1]. This material provides a unique example of a correlated electron system, where the interplay of charge and spin degrees of freedom results in a phase transition into a phase with coexistent spin gap and charge order. NaV_2O_5 is the only quarter-filled ladder compound known so far [2]. Each individual rung of the ladder is occupied by a single electron which is equally distributed between its left/right sites in the disordered phase (see figure 1). At $T_c = 34$ K this compound undergoes a phase transition when a spin gap opens, accompanied by charge ordering [3–6]. The experimentally observed two-dimensional (2D) long-range charge order in NaV_2O_5 [5, 6] (the ab-plane order is shown in figure 1) is *super-antiferroelectric* (SAF), as we have pointed out recently [7]. The theory of the spin–SAF transition put forward by us [7–9] is adequate in accounting for, even quantitatively, various aspects of the transition in NaV_2O_5. It deals, however, with a single (ab) plane, leaving aside the question of charge ordering along the third (c) direction. The phase transition in NaV_2O_5 quadruples the unit cell in the c-direction (the supercell of the ordered phase is $2a\times2b\times4c$), and the recent x-ray experiments [5, 6] revealed peculiar ordering patterns in c-direction (stacking order) of the super-antiferroelectrically charge-ordered planes. Here we present a model which provides the explanation for the observed stacking order in NaV_2O_5.

An insulating quarter-filled ladder system, with electrons localized on the rungs of the ladder, can be mapped on an effective spin–pseudospin model, where the Ising pseudospin ($\mathcal{T}^x$) represents left/right positions of the charge on a given rung, similar to the standard

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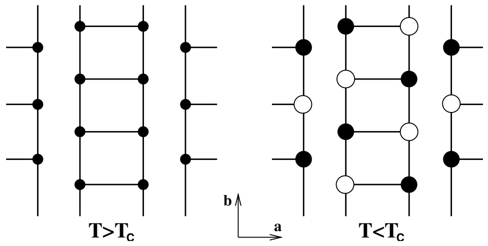

Figure 1. NaV_2O_5: ladders in the *ab*-plane. In the disordered phase each electron is equally distributed between left/right sites on a given rung (left panel), while below T_c electrons (filled black circles) order as shown in the right panel.

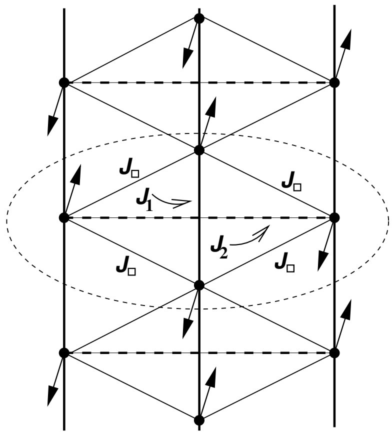

Figure 2. The *ab*-plane of coupled ladders mapped onto an effective 2D lattice. A vertical line and a dot represent a single ladder and its rung. The Ising pseudospin (up/down) represents the position (left/right) of the electron on a given rung.

pseudospin approach to the order–disorder-type phase transitions [10]. The 2D effective spin–pseudospin Hamiltonian, able to describe the spin–SAF transition in NaV_2O_5, was given in [7]. Since the present work is concerned with the physics of the charge order, we will discuss here exclusively the Ising sector of the full spin–pseudospin model.

Within the spin–pseudospin formalism, the *ab*-plane of coupled ladders can be mapped on the effective lattice shown in figure 2, which in its turn we smoothly map onto a more conventional square lattice. It is then easy to identify the charge order in the *ab*-plane (see figures 1 and 4) as the SAF phase [11] of the 2D nearest neighbour (nn) and next-nearest neighbour (nnn) Ising model, shown in figure 3. Since the Ising couplings $J_\sharp = J_\square$, J_1, J_2 originate from the Coulomb repulsion, we assume them to be antiferromagnetic (AF), i.e., $J_\sharp > 0$. SAF is the ground state of the 2D nn and nnn Ising model, if [7]

$$J_1 + J_2 > |J_\square|, \qquad \text{and} \qquad J_{1,2} > 0. \tag{1}$$

The SAF state can be viewed as two superimposed antiferromagnetically ordered sublattices (circled/squared sites shown in the right panel of figure 3), and it is four-fold degenerate, since each of these sublattices can be flipped independently.

Some possible patterns of the stacking charge order in NaV_2O_5, determined from the x-ray experiments [6], are shown in figure 4. In terms of the effective Ising model this translates into the 3D pseudospin ordering patterns depicted in figure 5. To explain the mechanism of these types of order, let us consider the 'minimal' 3D nn and nnn Ising model with the Hamiltonian

$$H = \frac{1}{2} \sum_{\mathbf{k},\mathbf{l}} J_{\mathbf{kl}} \mathcal{T}^x_{\mathbf{k}} \mathcal{T}^x_{\mathbf{l}} \tag{2}$$

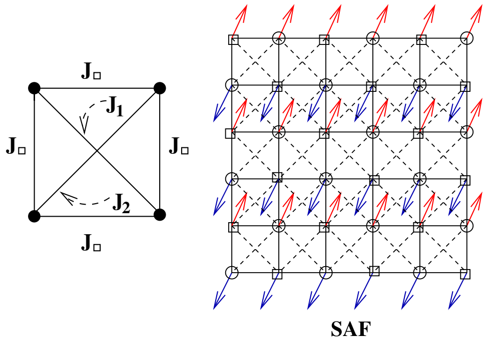

Figure 3. Couplings on an elementary plaquette of the 2D nn and nnn Ising model (left) and an example of the SAF order (right). An plaquette on the square lattice corresponds to the encircled region in figure 2.

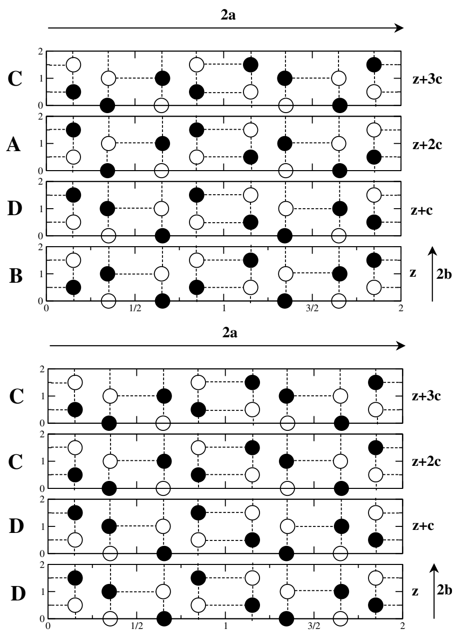

Figure 4. Possible patterns of the stacking charge order in NaV_2O_5 from the x-ray experiments (reprinted with permission from Grenier *et al* 2002 *Phys. Rev.* B **65** 180101(R). Copyright 2002 by the American Physical Society): ⟨**BDAC**⟩ (and ⟨**DBCA**⟩, not shown) (top); ⟨**DDCC**⟩ (and ⟨**BBAA**⟩, not shown) (bottom). Each layer (in the *ab*-plane) labelled by **A**–**D** corresponds to a particular realization of the four-fold degenerate SAF state.

where the bold variables denote lattice vectors. The sum includes spins on the nn sites coupled via $J_\square$, J_3 and on the nnn sites coupled via $J_{1,2,4}$ (cf figures 3, 5). This model reduces to a more familiar 3D ANNNI model [12] when the diagonal couplings $J_{1,2}$ are absent. We will be interested in the case of the plaquette couplings satisfying (1), i.e., when the planes are SAF-ordered in the ground state, and a frustrating nnn-interplane coupling $J_4 > 0$.

Note that the four patterns **A**–**D** of the SAF state can be divided into two pairs of the 'AF counterparts' (**A**, **B**) and (**C**, **D**) in the sense that in the presence of an AF coupling between two SAF-ordered planes, the counterparts **A** and **B** (or **C** and **D**) minimize the energy without inter-plane frustrations (cf figure 5).

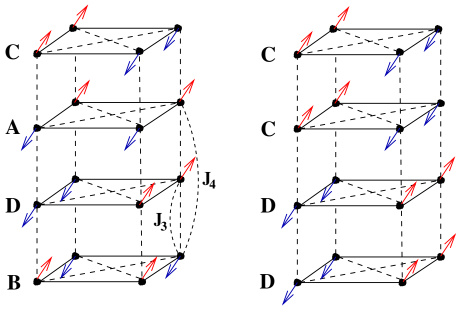

Figure 5. Two particular realizations of the 16-fold degenerate ground state of the 3D nn and nnn Ising model (2) at $J_4 > |J_3|/2$. The depicted Ising orders correspond to the charge ordering patterns shown in figure 4.

From energy considerations one finds that, if $J_4 > |J_3|/2$, the model has a 16-fold degenerate ground state composed of the SAF-ordered planes stacked with a period of four lattice spacings in the $z(c)$-direction. We will denote this 3D order as SAF $\times$ 4. (Note that the in-plane SAF phase itself can take either a 2×1 pattern, or a 1×2.) The number of frustrated inter-plane bonds (J_3) in the SAF $\times$ 4 phase is eight per four stacked elementary cubes of the lattice (in average two J_3-bonds per elementary cube). This phase can be realized via four four-fold degenerate stacking patterns:

$$\begin{array}{ll} \langle \mathbf{AABB} \rangle, & \text{type } \mathbf{I} \\ \langle \mathbf{ACBD} \rangle, & \text{type } \mathbf{II} \\ \langle \mathbf{ADBC} \rangle, & \text{type } \mathbf{III} \\ \langle \mathbf{CCDD} \rangle, & \text{type } \mathbf{IV}. \end{array}$$

Four-fold degeneracy of each of these stacking patterns comes from translations along the stacking direction, or, in terms of the above notations, from cyclic permutations inside the angular brackets. So, the two particular realizations of the SAF $\times$ 4 state shown in the left and right panels of figure 5 belong to the patterns **II** and **IV**, respectively.

If $J_4 < |J_3|/2$ the model can have two possible four-fold degenerate ground states, SAF $\times$ 1 or SAF $\times$ 2, depending on the sign of J_3. If the nn-interplane coupling is AF $J_3 > 0$, the model's ground state SAF$\times$2 can be realized via two two-fold degenerate stacking patterns $\langle \mathbf{AB} \rangle$ or $\langle \mathbf{CD} \rangle$. For a ferromagnetic nn-interplane coupling $J_3 < 0$, the four-fold degenerate ground state SAF $\times$ 1 is simply one of the four possible SAF patterns stacked in the c-direction. In each of the phases SAF $\times$ 1 or SAF $\times$ 2 there are four frustrated inter-plane bonds (J_4) per elementary cube of the lattice. Thus, to summarize the ground-state phases:

$$J_4 > |J_3|/2: \qquad \text{SAF} \times 4 \tag{3}$$

$$J_4 < J_3/2: \qquad \text{SAF} \times 2 \tag{4}$$

$$J_4 < -J_3/2: \qquad \text{SAF} \times 1. \tag{5}$$

The model (2), (3) provides the explanation for the charge ordering in NaV_2O_5 found in the most recent x-ray studies [6], carried out at ambient pressure deep in the ordered phase (at $T = 13$ K). Those authors found that the sum of patterns $\langle \mathbf{BDAC} \rangle + \langle \mathbf{DBCA} \rangle$ (i.e., $\langle \mathbf{II} + \mathbf{III} \rangle$ type) and/or of $\langle \mathbf{DDCC} \rangle + \langle \mathbf{BBAA} \rangle$ (i.e., $\langle \mathbf{IV} + \mathbf{I} \rangle$ type), makes the best fit to the scattering data, and not a single pattern. This implies that the actual stacking charge order in NaV_2O_5 accommodates all those (degenerate) patterns with stacking faults [5, 6].

An analysis of stacking faults between the various (totally 16) faultless patterns shows that they cost different energy. For instance, if $J_3 < 0$ the least energetically expensive (the energy is $(J_4 - |J_3|/2)N^2$ with respect to the ground state for $N \times N \times N$ lattice) are faults of type ⟨**II** or **III**⟩ • ⟨**I** or **IV**⟩, where • indicates the position of the fault. The examples are:

$$\begin{aligned}&\ldots\mathbf{ACBD}\bullet\mathbf{DCCD}\ldots\\&\ldots\mathbf{ADBC}\bullet\mathbf{AABB}\ldots.\end{aligned}\tag{6}$$

The faults of type ⟨**II** or **III**⟩ • ⟨**II** or **III**⟩, ⟨**I**⟩ • ⟨**I**⟩, ⟨**IV**⟩ • ⟨**IV**⟩, like, e.g.,

$$\begin{aligned}&\ldots\mathbf{ACBD}\bullet\mathbf{DACB}\ldots\\&\ldots\mathbf{ACBD}\bullet\mathbf{DBCA}\ldots\\&\ldots\mathbf{AABB}\bullet\mathbf{BAAB}\ldots\end{aligned}\tag{7}$$

cost twice as much energy as those of type (6). There are of course many other possible types of stacking faults (with higher energies) which we will not discuss. From an energy consideration, we can conclude that at low temperature faults of type (6) prevail. This result, together with the experimental findings [6], leads us to the conclusion that in NaV_2O_5 all four possible types of ordering (**I–IV**) occur indiscriminately, with minimal-energy stacking faults, e.g., ⟨**II**⟩ • ⟨**I**⟩ • ⟨**III**⟩ • ⟨**IV**⟩.

Above we assumed that $J_3 < 0$, which might appear odd, since all Ising couplings originate from the Coulomb repulsion, i.e., they are antiferromagnetic. In fact such ferromagnetic coupling is an effective coupling replacing interactions between several charges in order to keep the model 'minimal'[2]. In this sense J_4 is an effective coupling as well; both J_3 and J_4 should be viewed as phenomenological parameters whose signs and relative strengths are chosen to agree with experiments. We can however suggest a simple mechanism resulting in an effective $J_3 < 0$. Let us consider two nn ladders (two chains in terms of the effective lattice shown in figure 2) separated by a lattice unit c in the stacking direction. On a single plaquette in the bc-plane, let us take into account the nn couplings J_1 (along the (0, 1, 0)-direction) and $\tilde{J}_3$ (along the (0, 0, 1)-direction), with $J_1 > J_3$, in addition to an nnn coupling J_d along plaquette's diagonals (along (0, ±1, 1)-directions). A simple analysis shows that the two nearest stacked chains tend to align ferromagnetically in the c-direction when $J_d > \tilde{J}_3/2$. We can therefore take $J_3 = \tilde{J}_3 - 2J_d$ as the single *effective* nn coupling, as shown in figure 5. Considering the actual lattice distances in NaV_2O_5 and the distance dependence of the Coulomb repulsion, one finds $J_3 < 0$.

Experiments on NaV_2O_5 under pressure [13] show that the in-plane SAF charge order is robust and does not change, while at the pressure $P_c = 0.92$ GPa a transition of the ground state charge order from SAF × 4 into SAF × 1 occurs. Thus, in NaV_2O_5 the pressure dependence of in-plane couplings is 'non-critical', i.e., condition (1) is satisfied, while the ratio $\kappa \equiv J_4/J_3$ of the couplings between planes is more sensitive to pressure. As follows from (3), (5) this ratio reaches the frustration point $\kappa_c = -1/2$ at P_c, and then the ground state changes[3].

Another very interesting feature of the charge ordering under pressure in NaV_2O_5 is the existence of a region with numerous higher-order commensurate superstructures SAF × $\frac{m}{n}$ (where m, n are integers), i.e., a devil's staircase region above P_c on the temperature–pressure plane [13]. Ohwada and co-workers noticed a resemblance between the experimental phase diagram and that of the 3D ANNNI model. (For reviews on that model see, e.g., [12, 14].)

[2] For a single layer a 'truly minimal' model, still having the SAF phase, would be that with $J_\Box = 0$. In this case it consists of two decoupled superimposed (AF) Ising lattices. Then our model (2) with nn and nnn interactions between layers reduces to *two identical* interpenetrating decoupled 3D ANNNI models, cf figures 3, 5. Let us call this limit the A ⊗ A model for brevity.

[3] In connection to what was said before about J_3, we should point out that experiments do not rule out $J_3 > 0$ at ambient pressure since SAF × 4 order is insensitive to the sign of J_3, as long as (3) is satisfied. Then J_3 must decrease under pressure such that at P_c it is already ferromagnetic and $\kappa = \kappa_c$. We find such a possibility rather exotic, and will not consider it here. Note also that if $J_3 > 0$ at ambient pressure, the above analysis of energies of stacking faults should be modified accordingly.

However an explanation of the charge ordering in NaV_2O_5 in the framework of the ANNNI model is incorrect, as the latter cannot have the in-plane SAF order in principle. The minimal model to reproduce the observed experimental results is what we call the A $\otimes$ A model (see footnote 2): two superimposed square lattices create the observed overall SAF order in the individual layers, while the period of the charge order in the stacking direction is the same as in a single 3D ANNNI model.

Considering the geometry of the original NaV_2O_5 lattice, one can see that $J_\Box$ is indeed rather small in comparison to J_1,[4] so the minimal A $\otimes$ A model appears to be adequate for the description of the charge ordering in that compound.

The more complicated model (2) with $J_\Box \neq 0$ and (3) satisfied, is expected, from mean-field considerations, also to show a sequence of commensurate phases originated from the frustration point $\kappa_c = -1/2$ separating the SAF $\times$ 4 and SAF $\times$ 1 ground states, similar to the 3D ANNNI model. However, to substantiate this suggestion, a separate study of the temperature phase diagram of (2) is warranted.

So far we have been discussing the charge in NaV_2O_5 in terms of Ising models. The full spin–pseudospin Hamiltonian of the problem is more involved [7], since it also includes a transverse field in the Ising sector plus coupling of the charge (Ising pseudospin) to the spin degrees of freedom. The present 3D extension of the Ising sector can be treated along the lines of our earlier analyses [7, 8], resulting in the simultaneous appearance of the charge (Ising) order and spin gap.

Conclusions

We propose a mechanism for the stacking charge order in NaV_2O_5. It is a result of competition between couplings of the nearest and next-nearest planes with the four-fold degenerate SAF in-plane order. The simplest effective model resulting in the observed charge ordering patterns consists of two decoupled interpenetrating 3D ANNNI models (the A $\otimes$ A model).

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References

[1] For a review, see Lemmens P, Güntherodt G and Gros C 2003 *Phys. Rep.* **375** 1
[2] Smolinski H, Gros C, Weber W, Peuchert U, Roth G, Weiden M and Geibel C 1998 *Phys. Rev. Lett.* **80** 5164
[3] Isobe M and Ueda Y 1996 *J. Phys. Soc. Japan* **65** 1178
[4] Fujii Y, Nakao H, Yosihama T, Nishi M, Nakajima K, Kakurai K, Isobe M, Ueda Y and Sawa H 1997 *J. Phys. Soc. Japan* **66** 326
[5] van Smaalen S, Daniels P, Palatinus L and Kremer R K 2002 *Phys. Rev.* B **65** 060101
[6] Grenier S, Toader A, Lorenzo J E, Joly Y, Grenier B, Ravy S, Regnault L P, Renevier H, Henry J Y, Jegoudez J and Revcolevschi A 2002 *Phys. Rev.* B **65** 180101(R)
[7] Chitov G Y and Gros C 2004 *Preprint* cond-mat/0401295
[8] Chitov G Y and Gros C 2004 *Phys. Rev.* B **69** 104423
[9] Gros C and Chitov G Y 2004 *Preprint* cond-mat/0403263
[10] Blinc R and Žekš B 1974 *Soft Modes in Ferroelectrics and Antiferroelectrics* (Amsterdam: North-Holland)
[11] Fan C and Wu F Y 1969 *Phys. Rev.* **179** 560
[12] For a review, see Liebmann R 1986 *Statistical Mechanics of Periodic Frustrated Ising Systems* (Berlin: Springer)
[13] Ohwada K, Fujii Y, Takesue N, Isobe M, Ueda Y, Nakao H, Wakabayashi Y, Murakami Y, Ito K, Amemiya Y, Fujihisa H, Aoki K, Shobu T, Noda Y and Ikeda N 2001 *Phys. Rev. Lett.* **87** 086402
[14] Selke W 1988 *Phys. Rep.* **170** 213

[4] The same arguments suggest a weak diagonal J_2, which is, however, reinforced effectively due to the bilinear spin–pseudospin coupling in NaV_2O_5 [7].