

## Spin-Singlet Clusters in the Ladder Compound $\text{NaV}_2\text{O}_5$

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The space group of  $\alpha'$ - $\text{NaV}_2\text{O}_5$  turns below  $T_c = 34$  K from  $Pmmn$  with all V sites equivalent, into  $Fmm2$  with three independent vanadium sites per layer. This is incompatible with models of charge ordering into  $\text{V}^{4+}$  and  $\text{V}^{5+}$ . Our structure determination indicates that the phase transition consists of a charge ordering with three distinct valence states, formally  $\text{V}^{4+}$ ,  $\text{V}^{4.5+}$ , and  $\text{V}^{5+}$ . The singlet formation is not associated with dimerization on the spin ladder, but with the formation of spin clusters. Finally, we ascribe the quadrupling of the  $c$  axis to the large polarizability of the  $\text{V}_2\text{O}_5$  skeleton.

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Recently,  $\text{NaV}_2\text{O}_5$  was suggested [1] as a possible inorganic spin-Peierls system with a high ordering temperature of  $T_c = 34$  K, compared with 14 K for  $\text{CuGeO}_3$  [2]. A chainlike structure [3], a 1D antiferromagnetic Bonner-Fisher-like magnetization above  $T_c$ , and an isotropic exponential drop in the magnetization below  $T_c$  evidenced the spin-Peierls nature [1]. However, it was noticed that the compound has several characteristics distinctly different from spin-Peierls behavior. The entropy change at the transition is much larger than the expected value of  $k_B \ln 2$ , and the magnetic field dependence of  $T_c$  is too small [4,5]. These observations triggered further theoretical and experimental studies focusing on charge ordering as an alternative mechanism. Both approaches have used as the starting point a quarter-filled ladder compound, rendering the 1D characteristics. This ladder interpretation is pervasive in theoretical work [6–8], optical studies [9,10], and crystallographic work [3,11,12].

In this Letter we propose a different mechanism to account for both the magnetic spin-singlet formation and the charge ordering. Conventionally, the singlet is ascribed to antisymmetric coupling of two adjacent “rungs” of the ladder, i.e., two electrons on four vanadium atoms. However, we will show that the transition at 34 K involves the formation of a singlet state consisting of a larger entity: a plaquette consisting of six vanadium ions that contribute four electrons, distributed over three ladders. This singlet formation results in a charge ordering scheme with three distinct valence states for vanadium: 4+, 4.5+, and 5+ instead of the commonly assumed charge disproportionation into 4+ and 5+ only. Our conclusions are based on a detailed x-ray diffraction study at low temperature. Part of the conclusions are based on space-group considerations, and other results are based on the structural details of the structure determination.

Single crystals of  $\text{NaV}_2\text{O}_5$  were grown from the melt in gold crucibles as described in Ref. [13]. The single crystal diffraction was performed with an ENRAF-NONIUS CAD-4 diffractometer using  $\text{Mo-K}\alpha$  radiation and a He-flow cryostat. The measurements were performed 9 K below the transition temperature. The room temperature (RT) results are in complete agreement with our previous

report [14]. Below 34 K (LT) we observe the emergence of superlattice reflections indicating a doubling of the unit cell along both the  $a$  and the  $b$  axes, and a quadrupling of the  $c$  axis, implying a sixteenfold increase of the unit cell volume, in agreement with previous reports [15]. Within experimental error, the reflection intensities fulfill also below  $T_c$  orthorhombic symmetry. Moreover, the lattice is found to be  $F$  centered. This provides additional evidence that the LT symmetry is indeed orthorhombic, as  $F$  centering does not exist for monoclinic space groups. From the magnitude of the satellites one can estimate that the atomic displacements from the RT structure will be small (on average  $\sim 5$  pm). Because the RT structure does not contain pseudosymmetry, a second order phase transition cannot generate new symmetry elements. Therefore, the LT symmetry elements must be a subset of the RT set. Of the five orthorhombic  $F$  centered space groups, only space group  $Fmm2$ , with the twofold axis along  $c$ , fulfills this condition.

Despite the unambiguous space-group determination, the structure solution is not straightforward. The pseudo-symmetries result in large correlations between various atomic parameters. This was circumvented by Lüdecke *et al.* [12] by using, for a limited number of reflections, a superspace approach. This procedure is based on the premise that the crystallographic constraints between specific atomic parameters have a physically justifiable background. Here, we proceed with a conventional analysis, without such parameter constraints, based on a large number of high order reflections. In fact, our data set has no overlap with Lüdecke’s data, our lowest order reflections being already higher than Lüdecke’s highest order reflections. We will address a detailed comparison between the two approaches in a separate article [16].

We now proceed to see which models proposed thus far fulfill the requirements of the space group  $Fmm2$ . In Fig. 1 we display the essence of the following models: 1(A) Carpy and Galy [3], 1(B) Chatterji *et al.* [11], and 1(C) Mostovoy and Khomskii [8]. We can rephrase the space group  $Fmm2$  in the following  $\mathbf{a-b}$  plane criteria: (1) doubling along  $\mathbf{a}$  and  $\mathbf{b}$ , (2)  $F$  centering in the  $\mathbf{a-b}$  plane, and (3) mirror planes  $\perp \mathbf{a}$  and  $\perp \mathbf{b}$ . None of the

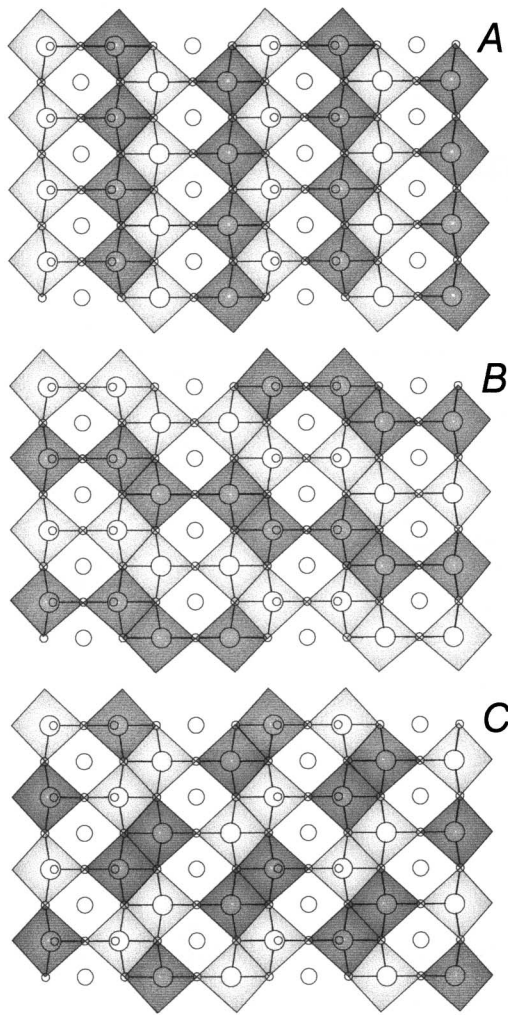


FIG. 1. Representation of the crystal structure of one  $\mathbf{a-b}$  plane of  $\text{NaV}_2\text{O}_5$ , highlighting three proposed charge ordering symmetries into  $\text{V}^{4+}$  and  $\text{V}^{3+}$  as suggested by Carpy and Galy (A), Chatterji *et al.* (B), and Mostovoy and Khomskii (C). Note that all three models and possible variations thereof lack elements of the  $Fmm2$  space group (see text).

above models, or variations thereof, fulfill all criteria and can therefore be discarded.

We can specify the structure in still more detail. Only half the mirror planes  $\perp \mathbf{a}$  and  $\perp \mathbf{b}$  survive the phase transition at 34 K. In the upper panel of Fig. 2 we display schematically several RT unit cells and indicate the two crystallographically different, and mutually excluding, possibilities: the choice for the  $mm$  site (defined at the intersection of mirrors  $\perp \mathbf{a}$  and  $\perp \mathbf{b}$ ) is either on a rung oxygen,  $\text{O}^*$ , or on a sodium. This yields two possibilities for filling the unit cell. The two alternatives differ in the number of Na and O atoms, but the number of V atoms equals three per plane in both cases. This implies the far-reaching conclusion that any physical model that describes the V states below  $T_c$  with less than three kinds of atoms per plane cannot represent the structure. This conclusion is based only on symmetry arguments. When comparing

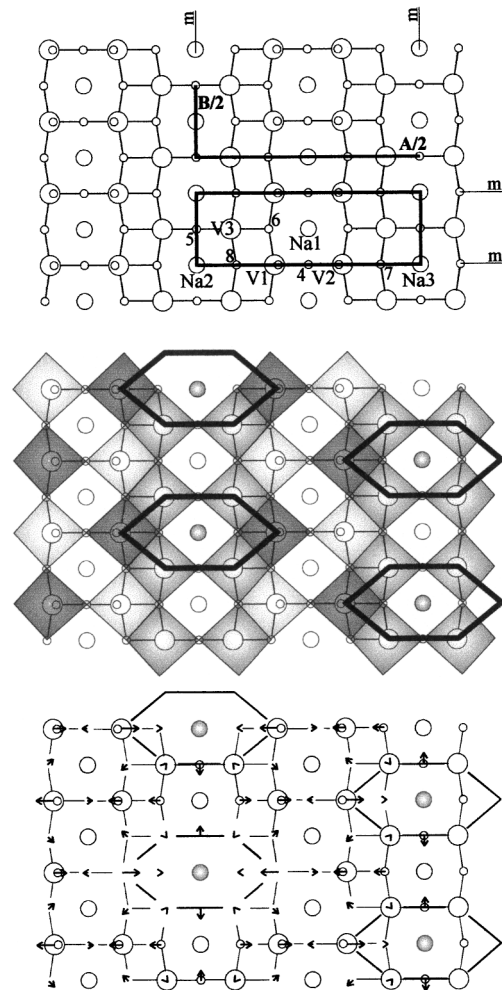


FIG. 2. Representations of the low temperature symmetry and structure of one of the two independent  $\mathbf{a-b}$  planes of  $\text{NaV}_2\text{O}_5$ . The upper panel shows the two possibilities for positioning the  $mm$  site of the irreducible unit on an oxygen (small circle) or on a Na (large unconnected circle). The latter possibility proved to be realized, and atomic numbering is given in this part of the figure, except for the apical oxygens  $\text{O}1$ ,  $\text{O}2$ , and  $\text{O}3$  of  $\text{V}1$ ,  $\text{V}2$ , and  $\text{V}3$ , respectively. Note that  $\text{Na}1$  lies on a bare twofold axis. The middle panel accentuates the charge ordering with dark  $\text{V}^{4+}$ , medium  $\text{V}^{4.5+}$ , and light  $\text{V}^{5+}$  basal plane pyramids, resulting in the formation of plaquettes around  $\text{Na}3$  (shaded). Note how this charge order illustrates the centering of the  $\mathbf{a-b}$  plane. The lower panel shows the atomic displacements, except for the apical oxygens, (multiplied by a factor of 25) within this basal plane. Note that all V distort towards the center of the plaquette, yielding  $d(\text{V}2-\text{V}3) = 302.7$  pm and  $d(\text{V}1-\text{V}3) = 304.8$  pm.

our results with published Na-NMR [17] and V-NMR data [18], we see that our results are more restrictive than the NMR data. NMR observed at least two Na sites and at least two V sites, as it cannot exclude the same hyperfine field for different positions.

In order to solve the structure, we generated a number of different sets of initial coordinates. We found that all sets with  $\text{Na}(2)$  at the  $mm$  site converged, whereas the sets

for  $O^*$  at the  $mm$  site did not. We conclude that  $Na(2)$  occupies the  $mm$  site with coordinates  $(0, 0, z)$ . The final isotropic refinement, for 28 free atomic coordinates per each of the two independent layers, resulted in  $R(F) = 0.0588$  for 2270 reflection data with  $F > 4\sigma(F)$ , and in  $R(F) = 0.0636$  for all 3261 data. The result of the refinement is shown in the lower panel of Fig. 2. We show the displacements of the atoms with respect to the undistorted  $Pm\bar{m}n$  symmetry, multiplied by a factor of 25, for the first layer. The second layer is practically identical (see below). Whereas the vanadium displacements are statistically most significant, we concentrate first on the oxygen displacements. We clearly identify three types of V-O basal plane pyramid changes in the first coordination sphere of V: a contraction, an expansion, and a rotation. Therefore, we assign the contracting pyramid containing V1 with a formal valence state  $V^{5+}$ , the expanding pyramid containing V2 with  $V^{4+}$ , and the rotating pyramid containing V3 with  $V^{4.5+}$ . The distortions are indeed small, and the maximum displacement of oxygen is only  $\sim 5$  pm. This model corresponds to the model mentioned by Riera and Poilblanc [19] and also suggested by Lüdecke *et al.* if we assign their modulated ladders with  $V^{4+}$  and  $V^{5+}$  and their unmodulated ladders with  $V^{4.5+}$ , respectively [12].

We now turn to the nature of the ordering at 34 K. Magnetic measurements indicate a singlet ground state. As the vanadium ions are occupied by, at most, one  $d$  electron, the singlets are formed from electrons that hop between sites. It was estimated that the largest hopping matrix elements occur between V coupled by O(4)/O(5) forming the rungs of the ladder,  $t_a \cong 0.35$  eV, and the V coupled by O(6)/O(7)/O(8) forming the posts of the ladder,  $t_b \cong 0.15$  eV [7]. This analysis resulted in a model that forms singlets by the dimerization of two adjacent rungs, each rung contributing one electron. In the valence assignment deduced above we could still form such a singlet. However, this assignment would leave free spin- $\frac{1}{2}$ 's on the  $V^{4+}$ , not observed experimentally. Furthermore, such a model would predict a V displacement along **b** (the post), not in agreement with our experimental observations. Our valence assignment suggests a completely different model. We propose to create singlets from one  $V^{4+}$  and two adjacent  $V^{4.5+}$  ions, contributing in total two electrons. This coupling leaves no free spins at low temperature. This possibility has been discarded in the literature because the  $90^\circ$  superexchange is small. However, the small V-V distance of 0.3 nm between V1-V3 allows direct exchange, estimated to yield  $t_{xy} \cong 0.3$  eV [7]. Considering that even larger hopping occurs on the rungs, we propose that the singlet consists of two of the aforementioned units forming a plaquette of six V atoms. This plaquette consists of two formal  $V^{4+}$  ions and four formal  $V^{4.5+}$  ions, contributing four electrons. This model deemphasizes the role of the ladders, but instead uses a description based on small magnetic spin-singlet clusters. The formation of the plaquette provides a straightforward explanation for the V displace-

ments along **a**, as the formal  $V^{4+}$  are pulled towards the center of the plaquette. Furthermore, the lower panel of Fig. 2 shows that all six V constructing the plaquette distort towards the center of the plaquette.

Whereas this Letter emphasizes the charge disproportionation  $V^{4+}-V^{5+}$  for half of the V, the charge transfer seems not complete. Using the bond valence sum method, we find that the amplitude of the charge modulation is limited to 0.2 electrons. As  $NaV_2O_5$  is isostructural to  $CaV_2O_5$  and similar to  $V_2O_5$ , a detailed comparison of the bond lengths can be made, which confirms the partial charge disproportionation. The charge disproportionation is reflected mostly in the V-O distances forming the rungs of the ladder (O4/O5). The resulting displacements are not restricted within the basal plane, but also significant along **c**, reflecting the 3D nature of this material. The magnetic singlet can be understood in the orbital ordering model described by Horsch and Mack [7] in a modified form. They described the ground state originating from  $d$  orbitals with  $d_{xy}$  symmetry coupled by an oxygen  $p_y$  orbital, coupling two rungs. The  $d_{xy}$  orbitals allow direct overlap between  $V^{4+}$  and its two  $V^{4.5}$ -like neighbors, forming the ends of the plaquette. Thus, the small singlet-triplet splitting can be understood in terms of the antisymmetric-symmetric combinations formed by coupling both  $V^{4+}$  ions to the center of the plaquette.

Finally, we focus on the stacking along the  $c$  axis. We observe a quadrupling of the lattice, notably a dimerization of dimers, as shown in Fig. 3. Layered structures are the exception for oxides, which usually prefer dense packed structures [20]. The relatively small nuclear charge of V yields a relatively large polarizable  $d$  orbital. This yields the very robust layered  $V_2O_5$  skeleton, which can be intercalated by monovalent (Li, Na, ...) and divalent (Mg, Ca, ...) cations, yielding a large class of compounds [21]. These structures can commonly lower their energy by distortions in the layers, such as a Peierls distortion, charge density waves, or clustering.

The structure refinement shows that the two crystallographically independent **a-b** planes exhibit almost identical displacements, and thus the same charge ordering. This plus the  $F$  centering result in a sequence along **c**: 5+, 5+, 4+, 4+, 5+, ... for the atoms on V1 and 4+, 4+, 5+, 5+, 4+, ... on V2. We can rationalize this result by observing that in this sequence each V1/V2-like ion is sandwiched by different valence states, i.e., each V experiences an electric field generated by its neighbors. Thus, the observed sequence maximizes the dipolar energy. The quadrupling along **c** can also be observed in the interatomic distances. The distance V-apical oxygen within the square pyramid is almost identical. However, the distance from the apical oxygen to the V of the next layer is observed as 315 pm (medium  $M1$ ), 323 pm (large  $L$ ), 316 pm (medium  $M2$ ), and 308 pm (small  $S$ ). The charge ordering sequence 5+, 5+, 4+, 4+, 5+, ... corresponds with distances  $M1-L-M2-S$ . The distances are

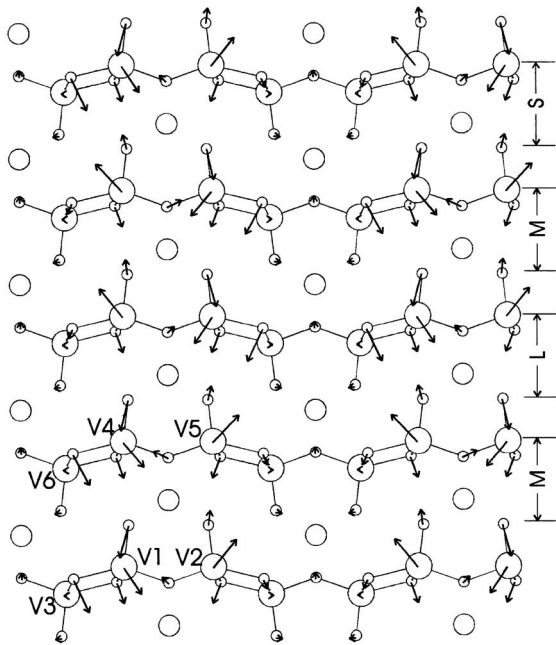


FIG. 3. Representation of the quadrupling of the  $c$  axis by showing the displacements (multiplied by a factor of 25) of  $\text{NaV}_2\text{O}_5$  within the  $a$ - $c$  plane ( $\frac{1}{2}\mathbf{B}$  thick). The distance of V to the next nearest apical oxygen exhibits a modulation: medium-long-medium-short-medium. . . ; whereas the distance of V to the nearest apical oxygen remains almost unchanged, reflecting the polar nature of  $\text{NaV}_2\text{O}_5$ .

not much affected if the V valence is the same in consecutive layers. However, there is a large difference (15 pm) between the sequence  $\text{V}^{4+}$  apical O- $\text{V}^{5+}$  and  $\text{V}^{5+}$  apical O- $\text{V}^{4+}$ , reflecting the polar nature of this structure. This large modulation in distances supports our suggestion that the polarizability is the driving force behind the quadrupling of the  $c$  axis.

In conclusion, the  $Fmm2$  low temperature structure of  $\text{NaV}_2\text{O}_5$  requires three different V sites per layer, which is incompatible with most existing models. Based on the oxygen displacement we assign these states with formal valence states  $\text{V}^{4+}$ ,  $\text{V}^{4.5+}$ , and  $\text{V}^{5+}$ . This assignment results in a description of the singlet ground state consisting of a plaquette of six vanadium ions, contributing four

electrons. The stacking of the singlets is governed by maximizing the polarization energy. Thus we observe in  $\alpha$ - $\text{NaV}_2\text{O}_5$  a remarkable interplay between the quantum-mechanical effect of singlet formation and the classical effect of polarizability.

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