Acentric Low-Temperature Superstructure of NaV_2O_5

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The low-temperature superstructure of α'-NaV_2O_5 is determined by synchrotron radiation x-ray diffraction. The high-temperature structure is confirmed to be centrosymmetric, but the modulated structure is found to be acentric $Fmm2$ on the $2a \times 2b \times 4c$ supercell. An analysis using superspace symmetry shows that there are modulated and nonmodulated chains of vanadium atoms, tentatively assigned to magnetic and nonmagnetic chains. The arrangement of these chains is different from any model previously considered. [S0031-9007(99)09001-8]

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An intensified interest in low-dimensional quantum systems was incited by the discovery of the first inorganic spin-Peierls compound $CuGeO_3$ [1]. The magnetic order corresponded to a superstructure comprising a dimerization of the copper atoms along the chains, with displacements of neighboring oxygen atoms through elastic coupling [2]. This model was in full accordance with a pairing of the spins on the copper chains. Modulations on neighboring chains were out of phase, thus explaining the second component of one-half of the modulation wave vector.

More recently, α'-NaV_2O_5 was found to exhibit a spin-Peierls transition at $T_{SP} = 34$ K [3]. Superstructure reflections in x-ray scattering were observed at $\vec{q} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{4})$ [4]. This was interpreted as a dimerization of chains of vanadium atoms along the $\vec{b}$ axis, whereby the other components of the modulation wave vector indicated the relative phases of the modulation in neighboring unit cells. The original interpretation assumed alternating chains of magnetic V^{4+} ions and nonmagnetic V^{5+} ions, with the superstructure to occur on the magnetic chains only. The discovery that the crystal structure at room temperature is centrosymmetric (space group $Pmmn$) questioned this interpretation, as only one type of vanadium atom is present in this symmetry [5–7]. Superstructures were proposed, assuming all vanadium atoms to be the same [7] and assuming alternating chains of vanadium atoms [8]. In the latter publication the presence of an inversion center in the crystal structure was questioned again.

Here we present the complete superstructure of α'-NaV_2O_5, as determined from x-ray scattering data measured at a temperature of 15 K. The superstructure is found to be acentric with space group $Fmm2$ on the $2a \times 2b \times 4c$ supercell. A superspace group analysis [9,10] identifies two types of chains of vanadium atoms, of which only one is modulated. However, the arrangement of the modulated and nonmodulated chains is different from any of the previously proposed models for the superstructure. The consequences are discussed for the possible locations of the spins and the nature of the spin-spin interactions.

NaV_2O_5 single crystals were grown by the flux method, as reported earlier [11]. A small piece of dimensions $0.02 \times 0.1 \times 0.05$ mm^3 was cut off and used for the x-ray scattering experiment with synchrotron radiation ($\lambda = 0.56$ Å) on beam line D3 of Hasylab at DESY-Hamburg. The sample was mounted on a closed-cycle helium cryostat on a four-circle Huber diffractometer and cooled down to $T = 15$ K. The lattice parameters of the basic-structure unit cell at 15 K were determined from the measured positions of 18 main reflections in the range $28° < 2\theta < 32°$. An orthorhombic lattice was found with $a = 11.2942(34)$ Å, $b = 3.6042(12)$ Å, and $c = 4.7545(15)$ Å.

Fuji *et al.* [4] reported satellite reflections at distances $\pm\vec{q}$ from the main reflections. This implies a F-centered $2a \times 2b \times 4c$ supercell for the superstructure. In a first experiment we tested the F centering by measuring all reflections of the $2a \times 2b \times 4c$ supercell within the range $24° < 2\theta < 28°$. Weak superstructure reflections were observed at positions corresponding to the F-centered lattice. Still much lower intensity was found at a few positions violating the F centering, but obeying a C centering. These reflections were too weak and too few to allow a structure refinement, and they were not considered in the remainder of the experiment.

Subsequently, we measured the intensities of the Bragg reflections of the F-centered supercell in a half-sphere in the range $6° < 2\theta < 45°$. After the usual corrections, the data were averaged in point group $mm2$, resulting in 872 unique reflections [543 observed reflections with $I > 2.5\sigma(I)$]. Using the 235 main reflections (231 observed ones) and the small unit cell, the basic structure in $Pmmn$ gave an excellent fit to the data with the final reliability factor $R = 0.0241$. The main reflections did obey the extinction conditions for the n glide and the two screw axes, and no deviations of the average structure from centrosymmetry could be detected.

For the superstructure we assumed that its symmetry is a subgroup of the high-temperature structure. This assumption is guided by the fact that the superstructure corresponds to small shifts of the atoms only, and the symmetry should be able to correctly describe the average positions of the atoms. It is then an easy exercise to derive that the screw axes along $\vec{a}$ and $\vec{b}$, as well as the n glide, are lost [9]. The proper orthorhombic space group for the supercell is thus $Fmm2$, and it is found that the modulated structure is acentric, despite the fact that the average structure in the modulated state remains centrosymmetric $Pmmn$. Indications for a still lower symmetry, such as Fm or $P\bar{1}$ were not found. The supercell with symmetry $Fmm2$ contains six independent vanadium atoms, of which the positions need to be determined (Table I). Direct refinement of the structure failed, because the parameters appeared to be too severely correlated.

The solution to this problem is provided by the superspace description of the structure [10]. Originally developed for incommensurately modulated structures [12], it also guides one towards the correct choice of parameters for commensurate modulations [13]. The diffraction pattern is indexed with four integer indices $(hklm)$ according to

$$\vec{S} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^* + m\vec{q}\,. \tag{1}$$

Main reflections have $m = 0$. Because of the commensurateness, the satellite reflections are restricted to $m = -1, 1, 2$. Analysis of the data on the four-indexing shows that there are 231 observed main reflections out of a total of 235, and 309 observed first-order satellites ($|m| = 1$) out of a total of 394. Of the 243 second-order satellites ($m = 2$), only one reflection has an intensity larger than $3\sigma(I)$ at $3.5\sigma(I)$. This value cannot be considered to be significantly different from 0, and within the limits of our experiment the second-order effect is found to be 0. The consequence for the structural analysis is that all second-order harmonics of the modulation functions have to be set equal to 0.

The positions of the atoms are described by their average values with respect to the unit cell of the basic structure and the values of the modulation functions [10]:

TABLE I. Positions of the independent atoms in the supercell in $Fmm2$ symmetry. Given are the relative coordinates of the average positions as well the shift in angstrom towards the actual positions in the modulated structure, as were derived from the refined modulation amplitudes [Table II, Eq. (2)]. The last column gives the magnitude of the shift (Å). Entries 0 are restricted to this value by the superspace symmetry. Wyckoff positions in $Fmm2$ are 8d: $(x, 0.375, z)$; 8c: $(0.125, y, z)$; 4a: $(0.125, 0.375, z)$; 16e: (x, y, z).

Atom	$\bar{x}_1$	$\bar{x}_2$	$\bar{x}_3$	u_1	u_2	u_3	Size
V1a	0.20110	0.125	0.09760	0	−0.000	0	0.000
V1b	0.20110	0.125	0.34760	0	−0.001	0	0.001
V2a	0.45110	0.375	−0.09760	−0.036	0	−0.039	0.053
V2b	0.95110	0.375	−0.09760	0.036	0	0.040	0.053
V2c	0.45110	0.375	0.15240	0.032	0	0.044	0.054
V2d	0.95110	0.375	0.15240	−0.031	0	−0.044	0.054
Nala	0.125	0.375	−0.03577	0	0	−0.004	0.004
Na1b	0.625	0.375	−0.03577	0	0	0.004	0.004
Na1c	0.125	0.375	0.21423	0	0	0.008	0.008
Na1d	0.625	0.375	0.21423	0	0	−0.008	0.008
Na2a	0.375	0.125	0.03577	0	0	0	0
Na2b	0.375	0.125	0.28577	0	0	0	0
O11a	0.125	0.125	0.12926	0	0.022	0	0.022
O11b	0.125	0.125	0.37926	0	0.023	0	0.023
O12a	0.375	0.375	−0.12926	0.028	0	0	0.028
O12b	0.375	0.375	0.12074	−0.017	0	0	0.017
O21a	0.28673	0.125	0.12195	0	0.014	0	0.014
O21b	0.28673	0.125	0.37194	0	0.019	0	0.019
O22a	0.03673	0.375	−0.12195	0.017	0	0.018	0.025
O22b	0.53673	0.375	−0.12195	−0.017	0	−0.018	0.025
O22c	0.03673	0.375	0.12806	−0.013	0	−0.019	0.023
O22d	0.53673	0.375	0.12806	0.013	0	0.019	0.023
O31a	0.19282	0.125	0.01316	0	−0.012	0	0.012
O31b	0.19282	0.125	0.26316	0	−0.016	0	0.016
O32a	0.44282	0.375	−0.01316	0.004	0	−0.036	0.036
O32b	0.94282	0.375	−0.01316	−0.004	0	0.036	0.037
O32c	0.44282	0.375	0.23684	−0.004	0	0.037	0.037
C32d	0.94282	0.375	0.23684	0.004	0	−0.036	0.037

TABLE II. Modulation amplitudes (Å) of the atoms as refined in the superspace symmetry $Pmm2(\frac{1}{2}, \frac{1}{2}, q_3)0ss$ [Eq. (3)]. Standard deviations are within parentheses. Entries given as 0 are restricted to this value by the superspace symmetry. The modulation amplitudes correspond to the atoms marked "a" in Table I.

Atom	A_1	A_2	A_3	B_1	B_2	B_3
V1	0	0.0011 (9)	0	0	−0.0002 (9)	0
V2	0.0472 (7)	0	0.0591 (4)	−0.0054 (10)	0	0
Na1	0	0	−0.0032 (17)	0	0	0.0081 (20)
Na2	0	0	0	0	0	0
O11	0	−0.0271 (51)	0	0	−0.0171 (52)	0
O12	−0.0304 (47)	0	0	−0.0121 (43)	0	0
O21	0	−0.0207 (33)	0	0	0.0125 (34)	0
O22	0.0180 (34)	0	0.0238 (23)	−0.0114 (30)	0	−0.0108 (26)
O31	0	0.0147 (39)	0	0	0.0138 (39)	0
O32	−0.0047 (34)	0	0.0446 (22)	0.0025 (33)	0	−0.0259 (21)

$$x_i = \bar{x}_i + u_i(\vec{q} \cdot \vec{r} + t) \tag{2}$$

for $i = 1, 2, 3$. $\vec{r} = (\bar{x}_1, \bar{x}_2, \bar{x}_3)$ are the average coordinates, and $u_i(\bar{x}_4)$ is the modulation function which has period 1 in its argument $\bar{x}_4 = \vec{q} \cdot \vec{r} + t$. The modulation functions are written as a Fourier expansion. Because of the missing second-order reflections, it is sufficient to include the first-order harmonics in the refinement:

$$u_i(\bar{x}_4) = A_i \sin(2\pi\bar{x}_4) + B_i \cos(2\pi\bar{x}_4)\,. \tag{3}$$

The symmetry of the modulated structure is described by the superspace group $Pmm2(\frac{1}{2}, \frac{1}{2}, q_3)0ss$, with $q_3 = \frac{1}{4}$. As for the supercell, the two screw axes and the n glide are incompatible with the modulation wave vector $(\frac{1}{2}, \frac{1}{2}, q_3)$, and they cannot occur as symmetry elements. Thus the center of symmetry is already lost for the average structure and there are two independent vanadium atoms (denoted by V1 and V2) with independent modulation functions. Because all atoms are on mirror planes, the superspace group results in symmetry restrictions on the modulation parameters, further reducing the number of parameters to be refined.

The modulation was determined by the refinement of all independent modulation amplitudes against the intensities of the main reflections and first-order satellites, using the computer program JANA98 [14]. The final result was independent of the choice of the starting model. The average coordinates were refined too, but with the additional restrictions of $Pmmn$ symmetry. Relaxing the restrictions towards the true symmetry of the average structure $Pmm2$ resulted in a set of dependent parameters. This shows again that in good approximation, the average structure remains centrosymmetric. Deviations from centrosymmetry are contained only in the modulation pattern. The final fit is excellent with $R = 0.0289$ for all observed reflections ($R = 0.0241$ for the main reflections and $R = 0.0618$ for the satellites). Modulation parameters are summarized in Table II.

The lack of a center of symmetry in the superspace group requires that the phase of the modulation be fixed at an arbitrarily chosen value along the $\vec{c}$ direction. To this end the cosine z amplitude of V1 was set equal to 0. Because of the commensurateness, there is but one value of t corresponding to the true structure [Eq. (2)]. Refinements for a series of values of t showed that the R value of the satellites varied smoothly between $R = 0.0618$ for the best fit at $t = 0.155$, and $R = 0.0629$ for the worst fit at $t = 0.030$. The set of modulation amplitudes was the same for all refinements. However, severe variations of the structure models were observed, as the values at which the modulation functions are sampled by the supercell are dependent on t. For $t = 0.030$ the supercell contained two modulated V2 atoms (V2a and V2b) and two nonmodulated V2 atoms. For $t = 0.155$, which was chosen as the best structure model, all four V2 atoms in the F-centered supercell have the same displacements within error limits (Table I).

Our refinement shows the major displacements to occur on the vanadium atoms, in accordance with models in which the origin of the modulation lies on these

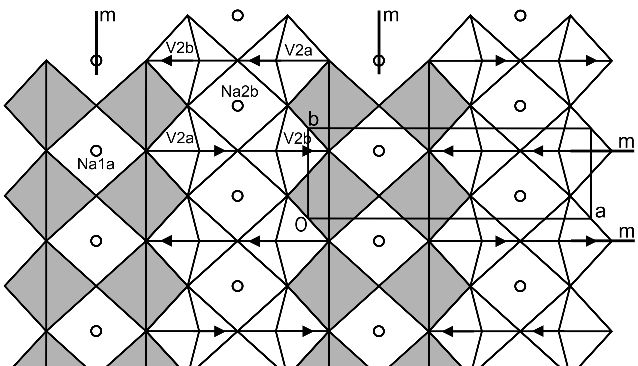

FIG. 1. Projection of the structure of NaV_2O_5 along $\vec{c}$. The unit cell of the basic structure is indicated. Gray and white polyedhra represent the two independent VO_5 pyramids in the $Pmm2$ symmetry of the basic structure. Arrows indicate the modulation of the vanadium atoms in the supercell; their sizes are 40 times the actual displacements. The positions of the mirror planes surviving in the $Fmm2$ supercell symmetry are indicated.

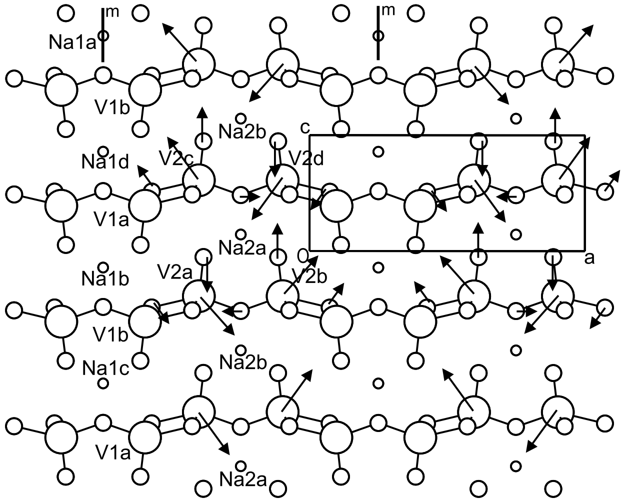

FIG. 2. Projection of the structure of NaV_2O_5 along $\vec{b}$. The modulations of the vanadium atoms as well as of the oxygen atoms are indicated by arrows, with sizes equal to 40 times the actual displacements. Large circles represent V atoms; small circles represent Na atoms; and intermediate circles represent O atoms.

atoms. The result shows that in the modulated state there are two types of chains of vanadium atoms. One of them (V2) is modulated and the other one (V1) is not modulated (Table II and Fig. 1). It appears that above T_{SP} only dynamic valence fluctations can exist, because all vanadium atoms are equivalent by symmetry. The magnetic ordering at T_{SP} should be considered as the driving force for the disproportion into magnetic V^{+4} and nonmagnetic V^{+5} atoms.

The basic structure can be considered as a collection of "ladders" with rungs V-O-V, which are all equivalent by the *Pmmn* symmetry of the basic structure [7]. The model for the superstructure derived here shows that there are modulated ladders and nonmodulated ladders alternating along $\vec{a}$, but segregated along $\vec{c}$ (Figs. 1 and 2). This excludes the possibility of a quarter-filled band [7], and each modulated ladder should contain two spins on each rung. The problem with this interpretation is that the expected dimerization of rungs is not observed (Fig. 2). Alternatively, one could assume that the modulation is due to charge ordering only. Then, the V1 atoms might form the magnetic ladders that are magnetically ordered without a structural distortion, in accordance with theories on the singlet state of a two-leg spin ladder.

Alternatively, the structure can be considered as a collection of chains of vanadium atoms along $\vec{b}$ [3,8]. The modulation should then represent a pairing of spins along this direction. The major difference with $CuGeO_3$ is that here the modulation of V atoms is purely transversal, whereas in $CuGeO_3$ the modulation of the Cu atoms is longitudinal [2].

The observed distortion pattern agrees well with the observed temperature dependence of the lattice parameters. The largest anomaly was observed in c as an anomalous expansion below T_{SP} [15]. This correlates with the largest atomic displacements along c. This is in contrast with $CuGeO_3$, where both the largest anomaly in the thermal expansion and the largest atomic displacements are parallel to the chain direction [2].

A detailed analysis of the superstructure shows that the atoms O22 and O32 move along with the vanadium atoms, whereas atoms O12 shift towards one of the two vanadium atoms on a modulated rung (Fig. 2). Alternately, along a rung and along $\vec{b}$ we thus find vanadium atoms with increased bonding and decreased bonding towards oxygen. This can be correlated with a possible charge ordering, in addition to and correlated with the magnetic ordering of the electron spins.

In conclusion, the superstructure of α'-NaV_2O_5 is determined in all its detail. It is found that a centrosymmetric average structure persists down to 15 K, but that the modulation pattern is essentially acentric. It is thus shown that there are modulated and nonmodulated chains of vanadium atoms parallel to $\vec{b}$, in accordance with models assuming magnetic (V^{4+}) [nonmagnetic (V^{5+})] chains. However, the arrangement of these chains is found to be different from any model previously considered, and a new analysis of the magnetic interactions in this compound is required.

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