Orthorhombic versus monoclinic symmetry of the charge-ordered state of NaV\textsubscript{2}O\textsubscript{5}

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High-resolution X-ray diffraction data show that the low-temperature superstructure of \(\alpha'\)-NaV\textsubscript{2}O\textsubscript{5} has an \(F\)-centered orthorhombic \(2a \times 2b \times 4c\) superlattice. A structure model is proposed, that is characterized by layers with zigzag charge order on all ladders and stacking disorder, such that the averaged structure has space group Fmm2. This model is in accordance with both X-ray scattering and NMR data. Variations in the stacking order and disorder offer an explanation for the recently observed devil’s staircase of the superlattice period along \(c\).

The low dimensional transition metal oxide \(\alpha'\)-NaV\textsubscript{2}O\textsubscript{5} undergoes a phase transition at a temperature of \(T_c = 34\) K. The transition is characterized by the development of both a nonmagnetic groundstate and a superstructure \(\mathbf{1}\). General agreement exists that the phase transition is associated with the development of charge order on the vanadium sublattice \(\mathbf{2}\), but the mechanism of the transition has not been revealed yet.

At room temperature \(\alpha'\)-NaV\textsubscript{2}O\textsubscript{5} crystallizes in space group Fmmm \(\mathbf{3}\). There is one crystallographically independent vanadium atom, that is in the mixed-valence state \(4.5+\). The structure can be considered as built of layers of two-leg ladders V\textsubscript{2}O\textsubscript{3}, that are stacked along \(c\), alternating with sodium atoms and additional oxygen. The lattice parameters of the basic structure at 15 K are \(a = 11.294\) \(\text{Å}\), \(b = 3.604\) \(\text{Å}\), and \(c = 4.755\) \(\text{Å}\) \(\mathbf{4}\). The superlattice below \(T_c\) can be described by an \(F\)-centered orthorhombic \(2a \times 2b \times 4c\) supercell. The superstructure was found to have symmetry Fmm2, but it showed two peculiar features \(\mathbf{5}\): (i) In one layer ladders with zigzag charge order alternate with ladders with vanadium in the mixed-valence state, (ii) Each of the two consecutive layers contains half of the six crystallographically independent vanadium atoms, but their structures were nearly equal. This crystal structure was found to be in agreement with two other X-ray diffraction measurements \(\mathbf{6}\).

Theoretical analyses have produced models that show zigzag charge order on all ladders \(\mathbf{7}\). However, most approaches did not consider the true supercell, and therefore they cannot be expected to reveal all aspects of the mechanism of the phase transition.

Various experiments, including anomalous X-ray scattering \(\mathbf{8}\), inelastic neutron scattering \(\mathbf{9}\), Raman spectroscopy \(\mathbf{10}\), and NMR \(\mathbf{11,12}\), have suggested zigzag charge order on all ladders. Such a model is at variance with the published crystal structure, and it is not possible for any ordered structure with Fmm2 symmetry \(\mathbf{13}\). Most notably, \(^{23}\)Na NMR has found eight resonances, that were interpreted as being due to eight crystallographically independent atomic sites, whereas the crystal structure in Fmm2 only has six independent Na sites. It was proposed that the true symmetry of the low-temperature structure might be a subgroup of Fmm2 corresponding to the loss of the F-center \(\mathbf{14}\). Alternatively, monoclinic symmetry was considered \(\mathbf{15}\).

In order to determine the true superstructure of NaV\textsubscript{2}O\textsubscript{5}, we have measured high-resolution, high-sensitive synchrotron radiation X-ray diffraction. The experiment indicates that the true superlattice is \(F\)-centered on the \(2a \times 2b \times 4c\) supercell. We show that an all zigzag charge order model with orthorhombic symmetry is possible assuming stacking disorder. This model is in agreement with both X-ray diffraction and NMR.

X-ray diffraction experiments were performed at beamline ID10A of the ESRF in Grenoble, France. Monochromatic radiation of a wavelength of \(\lambda = 0.66057\) \(\text{Å}\) was selected by the 220 reflection of diamond. Bragg reflections were measured by \(\omega\)-scans using a scintillation detector.

NaV\textsubscript{2}O\textsubscript{5} single crystals were grown by the flux method (batch number E106 \(\mathbf{16}\)). A crystal of dimensions 0.05 \(\times\) 0.06 \(\times\) 0.13 mm\(^3\) was mounted on a closed-cycle cryostat placed on a Huber diffractometer. The temperature was checked by measuring the intensity of a strong satellite reflection, that was found to be present for \(T < 33 \pm 1\) K only. The strong Bragg reflections could be indexed on the basis of the small primitive orthorhombic unit cell, in agreement with the literature.

A possible monoclinic distortion of the superlattice would result in a domain structure, that gives rise to split Bragg reflections, with the splitting angle equal to twice the deviation of the monoclinic angle from 90 deg. In order to test the hypothesis of a monoclinic lattice, a series of main reflections was measured at temperatures of both 20 K and 40 K. Because of limitations of the cryostat not all directions could be reached, but the measured reflections test any possible monoclinic distortion with the \(c\) axis as unique axis as well as most other possible lattice distortions. The profiles were found to broaden slightly below the phase transition, but splitting...
was not observed (Fig. 4). This limits a possible lattice distortion (e.g. monoclinic angle) to the Half Width at Half Maximum (HWHM) of the reflections, i.e. to 0.009 deg. Furthermore, the changes of profiles were also found for the (0,0,l) reflections (Fig. 1), that should have remained sharp for a monoclinic distortion with the c-axis as unique direction. Therefore, we conclude that the lattice is not monoclinic.

In a second experiment reflections corresponding to a primitive 2a × 2b × 4c supercell were measured at 20 K. Significant intensities were found for all eight measured first-order satellites as well as for all eight measured second-order satellites. Except for the forbidden (11,0,3) reflection, scattered intensity was not found for all measured 51 reflection positions that were forbidden by the F-center. However, the intensity of this forbidden reflection was the same at 20 K and 40 K, and its presence is not related to the phase transition. Presently we have achieved a much higher sensitivity towards weak scattering effects than in our previous experiment [8]. It is characterized by the ratio of the intensity of 25000 counts/s in the maximum of the (−21, 3, 5) first-order satellite and the intensity of 6 counts/s in the background.

In view of these results, we have re-analyzed the low-temperature structure assuming various symmetries of the F-centered 2a × 2b × 4c supercell. The data by Bernert et al. [1] appear to form the most complete set, and they have been used for all refinements presented here. In addition to data averaged in mm2 Laue symmetry (denoted as orthorhombic data), we have used the same intensities averaged in point group 1 (triclinic data).

Refinement of the orthorhombic superstructure (space group Fmm2) against orthorhombic data reproduced the model by Lüdecke et al. [5]. The same structure is obtained from the refinement of the orthorhombic model against the triclinic data, although the R value now is higher (Table 5). Assuming twinning, refinements with structure models according to F112/d or F11d (standard settings A2/a and Aα) gave R factors that were higher than for the Fmm2 structure.

Refinement of the monoclinic structure with space group F112 (standard setting A2) against triclinic data leads to R = 0.074 and a volume ratio of the twins equal to 0.75. The modulation of the V2 type of atoms is slightly smaller than in the Fmm2 model, while the V1 type of atoms have shifts of less than one third of the shifts of the V2 type atoms (Fig. 3). This model does not meet the requirements of similar zigzag charge order on all ladders. Most likely, the shifts of the V1 type atoms represent a fit to errors in the data. A structure with all ladders equal is obtained by setting the shifts of the V1 type atoms equal to those of the V2 type atoms. The refinement now converges at R = 0.082 and a twin volume ratio of 0.98. Almost perfect correlations are found between the parameters. It thus appears that an infinite number of monoclinic structure models give the same fit to the data as the orthorhombic structure Fmm2, including a monoclinic structure F112 with equal zigzag charge order on all ladders.

Assuming four twin domains, refinements in triclinic F1 symmetry converged at R = 0.075, with zigzag charge order on all ladders. Thus a better fit to the data was obtained than in the orthorhombic structure model. There are eight crystallographically independent vanadium atoms, but there are only four independent sodium atoms. Despite the good fit to the diffraction data, this model is not in agreement with the observations made by NMR [8].

The only possibility for complete zigzag charge order within the orthorhombic symmetry is disorder. For this, we consider the superstructure of a single layer as given by Mostovoy and Khomsky [5]. Given the 2a × 2b supercell, there are four equivalent realisations of this superstructure, that we denote by A, B, C, and D in a manner similar to the notation for different stacking sequences of a close packed structure of spheres (Fig. 2). If we superimpose a layer A with either C or D, an averaged structure results in which every other ladder is non-modulated. This averaged structure precisely is the structure of a single layer within the refined Fmm2 superstructure model [8]. Thus a disordered stacking of Layers A and C (or equivalently A and D, B and C or B and D) results in a structure with an average unit cell 2a × 2b × c in which the structure of the single layer corresponds to the observed structure of the individual layers. Of course, this model of stacking disorder is too simple, as it does not explain the observed quadrupling of the c lattice parameter.

Stacking faults can be considered within an ordered superstructure with orthorhombic symmetry Ccc2 on the 2a × 2b × 4c supercell. Possible stacking sequences in Ccc2 are ADCB and ABCD, whereby we have imposed the condition that neighboring layers must be different. A sequence with one stacking fault can be

...ADCB ADCB*DABC DABC...
that the stacking disorder given above is just one example of how the observed average structure can be obtained.

The true modes of stacking disorder should follow from the analysis of diffuse scattering or theoretical modelling.

The proposed stacking disorder of layers with full zigzag charge order is in agreement with all available experimental data. It explains both X-ray diffraction data and NMR. The reasons for the stacking disorder will lie in the multiple minima of the superstructure, and the resulting frustration. Considering nearest neighbor will lie in the multiple minima of the superstructure, and the notion of different stacking sequences with nearly equal energies offers an explanation for the recently observed variation of the superlattice length along $\vec{c}$. The different superstructures observed when applying hydrostatic pressure are to be considered as the result of different stacking sequences.

In conclusion, we have found that the true global symmetry of the low-temperature superstructure of NaV$_2$O$_5$ is Fmm$2$ on a $2a \times 2b \times 4c$ supercell. From the X-ray data, there is no direct evidence for another structure model than the fully ordered superstructure with alternatingly charged ordered and mixed valence ladders as given in Ref. [23]. A monoclinic distortion is ruled out, while the ordered structure with triclinic symmetry did not explain the NMR data of Refs. [20,21]. In order to accommodate observations by experimental techniques other than X-ray scattering, we propose that the true superstructure might be composed of layers with zigzag charge order on all ladders, that shows stacking disorder within a superstructure of orthorhombic symmetry, e.g. within a model with the space group $Ccc2$. This model explains all presently available experimental information. Furthermore, it provides an explanation for the observation of the devil's staircase behavior of the superlattice parameter along $\vec{c}$ under pressure. Finally it is noted, that the presence of stacking disorder in the superstructure might be the origin of the non-standard value of the critical exponent of the order parameter [21-23], and of the splittings observed in the anomaly of the heat capacity at the phase transition [24].

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FIG. 1. Intensity against crystal orientation ($\omega$–scan) for selected main reflections measured below and above the phase transition. (a) The $(-16,0,0)$ reflection; (b) $(-4,2,4)$; (c) $(0,0,8)$. Note that reflection indices refer to the supercell.

FIG. 2. The projection of one layer of the superstructure of NaV$_2$O$_5$ with charge order according to [3]. The $2a \times 2b$ supercell is indicated. Large filled and open circles represent vanadium atoms in the $4+\delta$ and $5-\delta$ valence states, respectively [9]. Small circles represent oxygen atoms. (a) Position A of the charge order. Position B is obtained from A by a shift over b (half the superlattice constant). (b) Position D of the charge order, that is related to A by a shift over b of the V1 type ladders only. Position C is related to A by a shift over b of the V2 type ladders only.

TABLE I. Partial reliability factors (R-factors) between observed and calculated superlattice reflections for various structure models and two data sets. Lower values indicate better agreements.

| Structure model | orthorhombic data | triclinic data |
|-----------------|-------------------|----------------|
| $F_{mm}$        | 0.063             | 0.082          |
| $F_{112/d}$ (twinned) | 0.138             | 0.145          |
| $F_{11d}$ (twinned) | 0.121             | 0.129          |