PHYSICAL REVIEW B, VOLUME 65, 060101(R)

Orthorhombic versus monoclinic symmetry of the charge-ordered state of NaV_2O_5

Sander van Smaalen,* Peter Daniels, and Lukas Palatinus
Laboratory for Crystallography, University of Bayreuth, D-95440 Bayreuth, Germany

Reinhard K. Kremer
Max Planck Institute for Solid State Research, Heisenbergstrasse 1, D-70569 Stuttgart, Germany
(Received 3 August 2001; published 15 January 2002)

High-resolution x-ray diffraction data show that the low-temperature superstructure of α'-NaV_2O_5 has an F-centered orthorhombic $2a\times2b\times4c$ 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.

DOI: 10.1103/PhysRevB.65.060101 PACS number(s): 61.50.Ks, 61.44.Fw, 61.66.Fn, 75.30.Fv

I. INTRODUCTION

The low dimensional transition metal oxide α'-NaV_2O_5 undergoes a phase transition at a temperature of $T_c=34$ K. The transition is characterized by the development of both a nonmagnetic ground state and a superstructure.[1,2] General agreement exists that the phase transition is associated with the development of charge order on the vanadium sublattice,[3,4] but the mechanism of the transition has not been revealed yet. See Ref. 5 for an overview of the literature.

At room temperature α'-NaV_2O_5 crystallizes in space group $Pmmn$.[6–8] 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_2O_3, that are stacked along $\vec{c}$, alternating with sodium atoms and additional oxygen. The lattice parameters of the basic structure at 15 K are $a=11.294$ Å, $b=3.604$ Å, and $c=4.755$ Å.[9] The superlattice below T_c can be described by an F-centered orthorhombic $2a\times2b\times4c$ supercell. The superstructure was found to have symmetry $Fmm2$, but it showed two peculiar features:[9,10] (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.[11,12]

Theoretical analyses have produced models that show zigzag charge order on all ladders.[3,4,13–17] 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,[18] inelastic neutron scattering,[19] Raman spectroscopy,[20] and NMR,[21,22] 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.[9] 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.[22] Alternatively, monoclinic symmetry was considered.[20]

In order to determine the true superstructure of NaV_2O_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 $2a\times2b\times4c$ 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.

II. EXPERIMENTAL

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

NaV_2O_5 single crystals were grown by the flux method [batch number $E106$ (Ref. 5)]. A crystal of dimensions $0.05\times0.06\times0.13$ 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 $T<33\pm1$ 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 a maximum 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

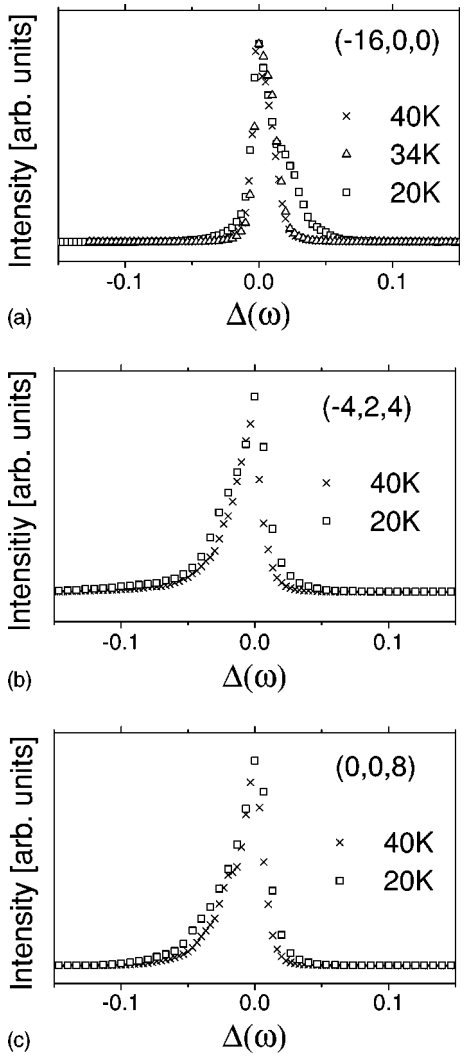

FIG. 1. Intensity against crystal orientation (ω scan) for selected main reflections measured below and above the phase transition. (a) The $(-16,0,0)$ reflection; (b) $(-4,2,4)$; (c) $(0,0,8)$. Note that reflection indices refer to the supercell.

were found to broaden slightly below the phase transition, but splitting was not observed (Fig. 1). 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(c)], that should have remained sharp for a monoclinic distortion with the c-axis as unique direction. Therefore, the observed changes in reflection profiles are either the result of a triclinic distortion, or an indication for strain caused by the structural rearrangements at the phase transition.

In a second experiment reflections corresponding to a primitive $2a\times 2b\times 4c$ supercell were measured at 20 K. Significant intensities were found for all eight measured first-order satellites ($l=4n\pm 1$ with n an integer) as well as for all eight measured second-order satellites ($l=4n+2$). On the average, the latter were three orders of magnitude weaker than the first-order satellites. Except for the forbidden $(11,0,3)$ reflection, scattered intensity was not found for

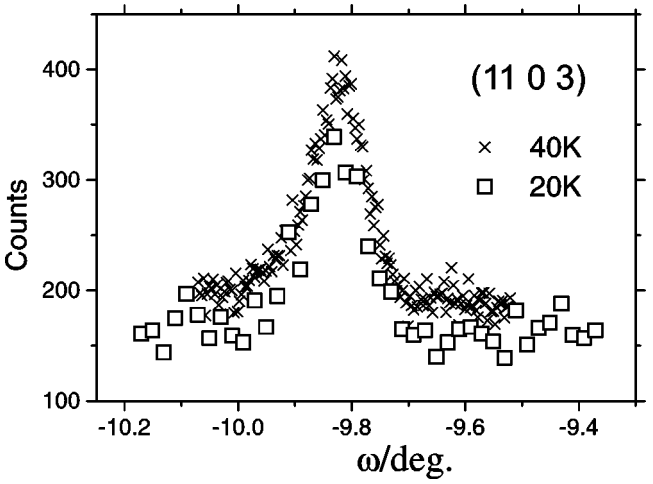

FIG. 2. Intensity against crystal orientation (ω scan) for the forbidden reflection $(11,0,-3)$ as measured at 20 K (squares) and at 40 K (crosses). Note the different levels of the background at 20 K and 40 K, in accordance with Ref. 24.

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 (Fig. 2), 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.[9] 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.

III. VANADIUM CHARGE ORDER AND STACKING DISORDER

In view of our new observations, we have reanalyzed the low-temperature structure assuming various symmetries of the F-centered $2a\times 2b\times 4c$ supercell. The data by Bernert *et al.* (Ref. 12) appear to form the most complete set, and they have been used for all refinements presented here. In addition to data averaged in mmm Laue symmetry (denoted as orthorhombic data), we have used the same intensities averaged in point group $\bar{1}$ (triclinic data).

Refinement of the orthorhombic superstructure (space group $Fmm2$) against orthorhombic data reproduced the model by Lüdecke *et al.*[9] The same structure is obtained from the refinement of the orthorhombic model against the triclinic data, although the R value now is higher (Table I). Assuming twinning, refinements with structure models ac-

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
$Fmm2$	0.063	0.082
$F112/d$ (twinned)	0.138	0.145
$F11d$ (twinned)	0.121	0.129

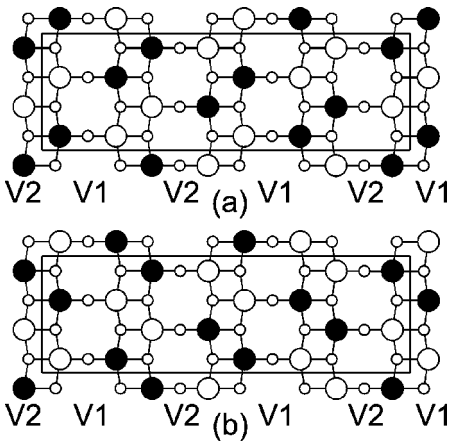

FIG. 3. The projection of one layer of the superstructure of NaV_2O_5 with charge order according to (Ref. 3). The $2a\times 2b$ supercell is indicated. Large filled and open circles represent vanadium atoms in the $4+\delta$ and $5-\delta$ valence states, respectively (Ref. 10). Small circles represent 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.

cording to $F112/d$ or $F11d$ (standard settings $A2/a$ and Aa) 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).[9] 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 $F\bar{1}$ 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.[21,22]

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.[3] Given the $2a\times 2b$ supercell, there are four equivalent realizations 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. 3). If we superimpose a layer **A** with either **C** or **D**, an averaged structure results in which every other ladder is nonmodulated. This averaged structure precisely is the structure of a single layer within the refined $Fmm2$ superstructure model.[9] 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 $2a\times 2b\times c$ 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 $2a\times 2b\times 4c$ 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

$$\cdots\mathbf{ADCB\ ADCB}\bullet\mathbf{DABC\ DABC}\cdots$$

where a dot $\bullet$ denotes the position of the stacking fault. On the average this structure has a $2a\times 2b\times 4c$ supercell with stacking sequence

$$\langle\mathbf{A},\mathbf{D}\rangle\langle\mathbf{D},\mathbf{A}\rangle\langle\mathbf{C},\mathbf{B}\rangle\langle\mathbf{B},\mathbf{C}\rangle,$$

where $\langle\mathbf{A},\mathbf{D}\rangle$ denotes one layer with a structure that is the average of the structures of the layers **A** and **D**, and $\langle\mathbf{A},\mathbf{D}\rangle=\langle\mathbf{D},\mathbf{A}\rangle$. This averaged structure precisely is the structure with space group $Fmm2$ as previously reported in.[9] Because the Bragg reflections in x-ray scattering reflect only the averaged structure, a model of layers with zigzag charge order on all ladders, but with the appropriate stacking disorder is in complete accordance with the measured diffraction intensities. Refinements with shifts of the V1 type atoms according to this disorder model indeed gave the same *R* values as the ordered $Fmm2$ model. The lattice is orthorhombic, and the disorder model is in accordance with our failure to observe any splitting of Bragg reflections. It is noticed, 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 modeling.

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 contacts only, the layer structures **A**, **B**, **C**, and **D** are equally probable, and stacking sequences **AD**, **AC**, **BD**, and **BC** have the same energy. The notion of different stacking sequences with nearly equal energies offers an explanation for the recently observed variation of the superlattice length along $\vec{c}$.[23] The different superstructures observed when applying hydrostatic pressure are to be considered as the result of different stacking sequences, as was also noticed in Ref. 23.

IV. CONCLUSIONS

We have found that the true global symmetry of the low-temperature superstructure of NaV_2O_5 is $Fmm2$ 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 charge ordered and mixed valence ladders as given in Ref. 9. A monoclinic distortion is ruled out, while the ordered structure with triclinic symmetry did not explain the NMR data of Refs. 21 and 22. 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 devils 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 nonstandard value of the critical exponent of the order parameter,[24,25] and of the splittings observed in the anomaly of the heat capacity at the phase transition.[5]

ACKNOWLEDGMENTS

X-ray scattering experiments were performed at beamline ID10A of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France (Experiment Number HS-1427). We gratefully acknowledge the assistance of the beamline staff, and in particular of Dr. F. Zontone. We thank E. Brücher for help with the crystal growth, and T. Chatterji for making his scattering data available. Financial support was obtained from the German Science Foundation (DFG) and the Fonds der Chemischen Industrie (FCI).

*Email address: smash@uni-bayreuth.de

[1] M. Isobe and Y. Ueda, J. Phys. Soc. Jpn. **65**, 1178 (1996).
[2] Y. Fujii, H. Nakao, T. Yoshihama, M. Nishi, K. Nakajima, K. Kakurai, M. Isobe, Y. Ueda, and H. Sawa, J. Phys. Soc. Jpn. **66**, 326 (1997).
[3] M. Mostovoy and D.I. Khomskii, cond-mat/9806215 (unpublished).
[4] H. Seo and H. Fukuyama, J. Phys. Soc. Jpn. **67**, 2602 (1998).
[5] D.C. Johnston, R.K. Kremer, M. Troyer, X. Wang, A. Klumper, S.L. Bud'ko, A.F. Panchula, and P.C. Canfield, Phys. Rev. B **61**, 9558 (2000).
[6] H.G. von Schnering, Y. Grin, M. Kaupp, M. Somer, R.K. Kremer, O. Jepsen, T. Chatterji, and M. Weiden, Z. Kristallogr. **213**, 246 (1998).
[7] A. Meetsma, J.L. De Boer, A. Damascelli, J. Jegoudez, A. Revcolevschi, and T.T.M. Palstra, Acta Crystallogr., Sect. C: Cryst. Struct. Commun. **54**, 1558 (1998).
[8] H. Smolinski, C. Gros, W. Weber, U. Peuchert, G. Roth, M. Weiden, and C. Geibel, Phys. Rev. Lett. **80**, 5164 (1998).
[9] J. Lüdecke, A. Jobst, S. van Smaalen, E. Morre, C. Geibel, and H.G. Krane, Phys. Rev. Lett. **82**, 3633 (1999).
[10] S. van Smaalen and J. Lüdecke, Europhys. Lett. **49**, 250 (2000).
[11] J.L. de Boer, A. Meetsma, J. Baas, and T.T.M. Palstra, Phys. Rev. Lett. **84**, 3962 (2000).
[12] A. Bernert, T. Chatterji, P. Thalmeier, and P. Fulde, Eur. Phys. J. B **21**, 535 (2001).
[13] J. Riera and D. Poilblanc, Phys. Rev. B **59**, 2667 (1999).
[14] C. Gros and R. Valenti, Phys. Rev. Lett. **82**, 976 (1999).
[15] A.N. Yaresko, V.N. Antonov, H. Eschrig, P. Thalmeier, and P. Fulde, Phys. Rev. B **62**, 15 538 (2000).
[16] P. Thalmeier and A.N. Yaresko, Eur. Phys. J. B **14**, 495 (2000).
[17] A. Langari, M.A. Martin-Delgado, and P. Thalmeier, Phys. Rev. B **63**, 144420 (2001).
[18] H. Nakao, K. Ohwada, N. Takesue, Y. Fujii, M. Isobe, Y. Ueda, M. von Zimmermann, J.P. Hill, D. Gibbs, J.C. Woicik, I. Koyama, and Y. Murakami, Phys. Rev. Lett. **85**, 4349 (2000).
[19] B. Grenier, O. Cepas, L.P. Regnault, J.E. Lorenzo, T. Ziman, J.P. Boucher, A. Hiess, T. Chatterji, J. Jegoudez, and A. Revcolevschi, Phys. Rev. Lett. **86**, 5966 (2001).
[20] M.J. Konstantinovic, Z.V. Popovic, A.N. Vasilev, M. Isobe, and Y. Ueda, Solid State Commun. **112**, 396 (1999).
[21] Y. Fagot-Revurat, M. Mehring, and R.K. Kremer, Phys. Rev. Lett. **84**, 4176 (2000).
[22] T. Ohama, A. Goto, T. Shimizu, E. Ninomiya, H. Sawa, M. Isobe, and Y. Ueda, J. Phys. Soc. Jpn. **69**, 2751 (2000).
[23] K. Ohwada, Y. Fujii, N. Takesue, M. Isobe, Y. Ueda, H. Nakao, Y. Wakabayashi, Y. Murakami, K. Ito, Y. Amemiya, H. Fujihisa, K. Aoki, T. Shobu, Y. Noda, and N. Ikeda, Phys. Rev. Lett. **87**, 086402 (2001).
[24] S. Ravy, J. Jegoudez, and A. Revcolevschi, Phys. Rev. B **59**, 681 (1999).
[25] B.D. Gaulin, M.D. Lumsden, R.K. Kremer, M.A. Lumsden, and H. Dabkowska, Phys. Rev. Lett. **84**, 3446 (2000).