X-ray anomalous scattering investigations on the charge order in $\alpha'$-NaV$_2$O$_5$

S. Grenier$^1$, A. Toader$^{1,*}$, J.E. Lorenzo$^{1,2}$, Y. Joly$^1$, B. Grenier$^3$, S. Ravy$^4$, L.P. Regnault$^4$, H. Renevier$^1$, J.Y. Henry$^5$, J. Jegoudez$^6$ and A. Revcolevschi$^5$

$^1$Laboratoire de Cristallographie, CNRS, BP 166, 38042 Grenoble cedex 9, France

$^2$European Synchrotron Radiation Facility, Av. Jules Horowitz, BP 220, 38042 Grenoble cedex 9, France

$^3$Commissariat à l’Energie Atomique, Département de Recherche Fondamentale sur la Matière Condensée, SPSMS/MDN, 38034 Grenoble cedex 9, France

$^4$Laboratoire de Physique des Solides, CNRS, Université Paris-Sud, Bât 510, 91405 Orsay cedex, France

$^5$Laboratoire de Physico Chimie des Solides, CNRS, UMR 8648, Université Paris-Sud, Bât 414, 91405 Orsay cedex, France

(August 17, 2019)

Anomalous x-ray diffraction studies show that the charge ordering in $\alpha'$-NaV$_2$O$_5$ is of zig-zag type in all vanadium ladders. We have found that there are two models of the stacking of layers along c-direction, each of them consisting of 2 degenerated patterns, and that the experimental data is well reproduced if the 2 patterns appears simultaneously. We believe that the low temperature structure contains stacking faults separating regions corresponding to the four possible patterns.

PACS numbers: 71.27.+a, 61.10.Eq, 61.50.Ah, 71.45.Lx

In the recent past years $\alpha'$-NaV$_2$O$_5$ has raised a great deal of interest as being the second inorganic compound, after CuGeO$_3$, where a quantum antiferromagnetic state is achieved at the expense of a lattice distortion [1]. At $T_C$=34K, it exhibits a structural [2] as well as a magnetic phase transition that lifts the magnetic degeneracy, opening an energy gap ($\Delta = 9.8$ meV) between the ground state, a non-magnetic spin-singlet, and the lowest magnetic spin-triplet [3]. NMR experiments [4] reported one opening of an energy gap ($\Delta = 9.8$ meV) between the ground state, a non-magnetic spin-singlet, and the lowest magnetic spin-triplet [3].

Below 34K, a set of weak diffraction peaks appear at (h, k, l) Bragg positions with an intensity being roughly $10^4$ times weaker than the Bragg peaks of the $Pmmn$ phase. The refinement of the low temperature (LT) crystal structure [5] has been greatly hindered by the large size of the supercell, $2a \times 2b \times 4c$, including 16 unit cells, and therefore, by the large number of atoms to consider. This problem has been circumvented by using a super-space approach, which allows to place some constraints between specific atomic parameters. They have shown that the $Pmmn$ phase remains almost unchanged, adjacent unit cells undergoing very small distortions and that the LT space group can be reasonably refined in $Fmm2$, a subgroup of $Pmmn$. They report even still weaker peaks obeying a C-centering, and therefore violating the F-centering, but these reflections have been discarded in the refinement due to their very low intensity. Later, de Boer and co-workers arrived at an identical conclusion by performing a conventional structure refinement on many measured reflections [6].

$\alpha'$-NaV$_2$O$_5$ can be seen as a set of layers of two-legs vanadium ladders running along the b-direction with the rungs along the a-direction. V are located inside oxygen squared-base pyramids whose corners are shared with neighbor pyramids. The cations Na$^+$ are located between the layers. The LT distortions, as determined by J. Lüdecke et al. [7], concerns the pyramids belonging to half of the ladders, indeed modulated and non-modulated ladders alternate along a-direction. The displacement highly concerns the “bridge oxygen”, at the center of the rung, that is shifted 0.07˚ towards one V of the rung, and alternatively to the other V in the next rungs of the ladder. These latter distortions suggest an alternated localization of the 3d electron on one side of the rung along the ladder.

The above structure determination has been questioned by experimental results issued from a wide variety of techniques. The $^{51}$V NMR study [8] has determined only two valence states; the Raman spectroscopy [9] measures a number of Raman modes not consistent with the number of possible modes in the $Fmm2$ structure. One of the most compelling results is probably $^{23}$Na NMR studies [10,11] reporting 8 inequivalent Na sites, again in complete disagreement with x-ray refinement. Neutron inelastic scattering [12] and anomalous x-ray scattering [13] results concluded on a zigzag pattern along all the v ladders, but only a single-layer model was considered.
in their calculations. It is interesting to note that these 2 structural methods have converged to a similar solution without using conventional crystallography methods, whereas purely crystallographic refinements are certainly hindered by the inherent complexity of the CO in $\alpha'$-NaV$_2$O$_5$. In this work we present the full charge disproportionation on all the ladders and the stacking sequence along the c-direction in $\alpha'$-NaV$_2$O$_5$ by means of anomalous x-ray diffraction.

Anomalous diffraction is a powerful tool in the determination of charge ordering as the X-ray resonant scattering amplitude of the atoms is related to the density of occupied and unoccupied electronic states. By tuning the X-ray energy through an absorption edge of the vanadium, a core electron is excited and virtually transits to outer unoccupied states. Below $T_C$, and as a result of the CO, we shall assume two new charge states. The anomalous scattering factor for each $V^{4+}$ and $V^{5+}$ carries out the information on the charge localization together with the "bridge" oxygen displacement. Under the assumption that the local atomic configuration is not much altered by this charge ordering, the resulting near-edge absorption spectra (see Fig. 1) will be slightly shifted towards lower ($V^{4+}$) or higher ($V^{5+}$) energies with no significant change in the near-edge structure (first 50 eV above the edge). This overall energy shift, amounting a few eV, is known as the chemical shift. Mathematically speaking, the above sentence implies that $f^{3+}(E+\delta E) \approx f^{3+}(E) \approx f^{4.5+}(E+\delta E)/2$. The measured absorption spectra corresponds to an average of all the atoms, and therefore $f(E) = f^{4.5+}(E)$. Appropriate spectra for $V^{4+}$ and $V^{5+}$ have been obtained through an adequate choice of $\delta E$.

As the energy dependence of the imaginary part of $f(E)$, $f''(E)$, typically shows a discontinuity in a step-like form (see Fig. 1), the chemical shift may yield dramatic anomalies if the anomalous factors of the two valence states are subtracted, as it occurs in x-ray diffraction experiments for some given, often very weak, reflections. Indeed, the scattering amplitude of the vanadium atom comes in multiplied by a phase factor $e^{i\mathbf{Q}\cdot\mathbf{r}}$ which, for suitable values of $\mathbf{Q}$ and $\mathbf{r}$, allows to put atoms with different valences in opposite phase. For such specifically chosen reflections, the vanadium partial structure factor is given by $F \propto f^{3+}(E) + e^{i\pi} f^{5+}(E) \approx f^{5+}(E + \delta E) - f^{5+}(E)$, proportional to the derivative with respect to energy of the anomalous scattering factor, $F \propto \partial f^{5+}/\partial E$. This is a very powerful property, exclusive to anomalous x-ray diffraction, and it has been used for compounds undergoing small distortions due to charge and/or orbital ordering.

An as-grown $\alpha'$-NaV$_2$O$_5$ high quality single crystal was used in this experiment. It was mounted on the cold finger of a closed cycle He refrigerator, and data collection were carried out at the base temperature, 13K. Experiments were performed at the ID20 beamline in the European Synchrotron Radiation Facility (Grenoble). An undulator provided the emission of a highly $\sigma$-polarized photon flux, the monochromatization was performed by a Si-(111) double crystal with an energy resolution less than 0.8 eV while mirrors located before and after the monochromator assembly were tuned to reject high energy harmonics. The scattering plane was vertical, and therefore the incident photon polarization state is $\sigma$. Measurement of the polarization components of the diffracted beam was possible by using the (004) reflection of a pyrolytic graphite analyzer crystal.

A total of 20 different diffraction peaks of the low temperature phase have been measured as a function of the incident photon energy, and under different polarization conditions. The energy step for all the scan is 0.5 eV. We have found that peaks having a strong anomalous contribution are $(9/2, 1/2, 0), (9/2, 1/2, 1), (11/2, 1/2, 0), (11/2, 1/2, 1)$, $(15/2, 1/2, 0)$ and $(15/2, 1/2, 1)$ which were measured with the polarization along the $b$-direction. In the following we shall use the notation $(h, k, \ell)_{(yz)}$ to indicate that the $(h, k, \ell)$ Bragg intensity has been measured with the polarization in the $b(c)$-direction.

Also were measured spectra with the polarization along $c$: the $(15/2, 1/2, 1)_z, (7, 0, 1)_z, (7, 1, 1/2)_z, (6, 0, 1/2)_z, (6, 1, 1/2)_z$ and also, the peaks $(p, 0, 0)_z$ with $p = 1, 3, 5, 7$ in $\sigma-\sigma$ and $\sigma-\pi$ geometries. The $(15/2, 1/2, 1)_z$ peak has a huge anomaly at 5466 eV (see Fig. 1 right panel), as Nakao et al. have also found. This result is in contrast with the result for $(15/2, 1/2, 1/2)_y$, where the peak at 5466 eV has completely disappeared (Fig. 1 left panel), thus revealing the phenominal polarization effects this compound exhibits . The other peaks did not show anomalous behavior except for the $(p, 0, 0)_z$ but in the $\sigma-\pi$ channel only. Indeed
(p, 0, 0)\textsubscript{z} peaks are extinct in the high temperature phase because of the \(n\)-glide plane, and one expect signal in the \(\sigma - \pi\) channel, alone. The lack of anomalous signal in \(\sigma - \sigma\) channel below \(T_C\) in the (p, 0, 0)\textsubscript{z} and in the (h, k, \(\frac{1}{2}\))\textsubscript{z} reflections is a key feature that we shall use below.

Reference fluorescence spectra were taken by removing the analyzer crystal and turning the crystal off the Bragg reflection by \(1^\circ\). The spectra were used to extract adequate values of \(f\) and \(f''\) (self-absorption correction has also been carried out) which already include geometrical corrections of the tensor form of the scattering factor.

The reflection \((\frac{15}{4}, \frac{1}{2}, \frac{1}{2})\) (in all measured polarizations) is of very special importance as the energy dependence of the scattered intensity clearly suggests a derivative effect (Fig. 1). If two vanadium atoms have the same valence but opposite phases their contribution would cancel out, whereas if the same atoms have different valence they will contribute to the derivative effect. For \((\frac{5}{2}, \frac{1}{2}, \frac{1}{2})\) Bragg peaks, adjacent cells along the \(a\)- and \(b\)-directions have a phase difference equals to \(\pi\). In the \(c\)-direction, the 4 layers have a phase difference equals to 0, \(\frac{\pi}{2}\), \(\pi\) and \(\frac{3\pi}{2}\), respectively. In other words, an atom in \(x, y, z\) is in opposite phase with atoms in \(x + \frac{1}{4}, y, z\), in \(x, y + \frac{1}{4}, z\), in \(x, y, z + \frac{1}{4}\) and in \(x + \frac{1}{4}, y + \frac{1}{4}, z + \frac{1}{4}\). Under this construction, the pair of atoms in a single rung has to have different valence state in order to keep the insulating state above \(T_C\). The first step of the valence attribution is shown in Fig. 2 (upper panel). The simple rule found in our spectra readily implies that the V-atoms of different valences have to be arranged in zigzag and excludes \(V^{4+}, V^{4+}\ldots\) chains along the \(b\)-direction.

For the \((6, 0, \frac{1}{4})\)\textsubscript{z} peak, no anomalous signal has been detected, and therefore all V-contributions to the structure factor have to cancel out. For this reflection, atoms on a same \((a, b)\)-plane have the same phase, whereas atoms in \(z + \frac{1}{4}\) are in opposite phase. Therefore, we infer that the second layer along \(c\)-direction should exhibit the same CO pattern as the first one, and identically between layers 3 and 4, as it is shown in Fig. 2 (lower panel).

Finally, an atom at \(x\) have a phase difference equals to \(\pi\) with respect to atoms in \(x + \frac{1}{4}\) for \((p, 0, 0)\)\textsubscript{p - odd} peaks. Extinction for these reflections immediately implies that
ladders centered at \( x = \frac{1}{4} \) have to be modulated as the one in \( x = \frac{1}{4} \), Fig. 3. By applying the above mentioned conditions, derivative in \( (\frac{15}{4}, \frac{1}{2}, \frac{1}{4}) \) and the absence of intensity in \( (6, 0, \frac{1}{4}) \) peak, to the ladders at \( x = \frac{1}{4} \) one get the patterns in Fig. 3. V-extinction considerations in the above set of Bragg reflections yield CO in all ladders and therefore rules out \( Fmm2 \) space group. The symmetry is of \( F2_1 \) type with 8 inequivalent sites for Na. Note that no fit has been needed so far.

At this stage of our deductions, we are confronted with the choice among 4 models: indeed the zigzag pattern on one ladder can be shifted along the \( b \)-direction relatively to the neighboring one, as shown in Fig. 3. Only the ladders centered at \( x = 0 \) and in \( x = \frac{1}{2} \) (and equally the ladders at \( x = \frac{1}{4} \) and \( x = \frac{3}{4} \)) are related to ensure the derivative effect. In order to proceed further we shall perform a detailed analysis of 3 different reflections: the already studied \( (\frac{5}{4}, \frac{1}{2}, \frac{1}{4}) \) (see Fig. 1) and \( (\frac{5}{4}, \frac{1}{2}, \frac{1}{4}) \) (see Fig. 1) and \( (\frac{5}{4}, \frac{1}{2}, \frac{1}{4}) \) (see Fig. 1).

The fit of reflections \( (\frac{9}{2}, \frac{1}{2}, \frac{3}{4}) \) and \( (\frac{9}{2}, \frac{1}{2}, \frac{3}{4}) \) shows that none of the BDAC or DDCC patterns of model 1 alone can reproduced both reflections, as it is shown in Fig. 4. The same occurs for the DDCC and BBAA patterns of model 2 (not shown). In order to obtain better values of the phases, \( V \)-atomic displacements along \( a \) and \( c \) have been introduced in the fit, but with the constraints imposed by the extinction conditions. Indeed the sum of patterns BDAC and (the complementary) DBCA of model 1 and, equally, the sum of patterns DDCC and AABB of model 2 perfectly accounts for the energy dependence of all measured reflections. In order to accommodate these findings, the actual low temperature structure of \( \alpha' \)-NaV\(_2\)O\(_5\) should contain either domains, related to the stabilization of a monoclinic structure, or stacking faults of model 1 or model 2 or of both together. The first solution implies the presence of splitted Bragg reflections, which have not been observed either in our experiments nor in Van Smaalen’s work [7], and therefore can be safely ruled out. The second solution implies a degenerated ground state which should give rise to very complicated phase diagrams. The x-ray diffraction results under pressure (and temperature) by Ohwada et al. [18] nicely show the development of a series of modulation wavevectors along the \( c \)-direction. This sequence, qualitatively understood within the framework of the Devil’s Staircase-type phase transitions, reflects the presence of competing arrangements along \( c \) of nearly degenerate units, as these proposed in this paper.

As a conclusion, our x-ray anomalous diffraction data has allowed to solve one of the most controversial and standing problems in the last years, the charge ordering standing problems, related to the stabilization of a monoclinic structure, or stacking faults of model 1 or model 2 or of both together. The first solution implies the presence of splitted Bragg reflections, which have not been observed either in our experiments nor in Van Smaalen’s work [7], and therefore can be safely ruled out. The second solution implies a degenerated ground state which should give rise to very complicated phase diagrams. The x-ray diffraction results under pressure (and temperature) by Ohwada et al. [18] nicely show the development of a series of modulation wavevectors along the \( c \)-direction. This sequence, qualitatively understood within the framework of the Devil’s Staircase-type phase transitions, reflects the presence of competing arrangements along \( c \) of nearly degenerate units, as these proposed in this paper.

FIG. 4. Experimental data (once corrected from absorption) for peaks \( (\frac{9}{2}, \frac{1}{2}, \frac{3}{4}) \), with \( \ell = 3 \) (left) and \( \ell = 5 \) (right) and results of simulations with model 1. Model 2 provides simulations of identical quality. Whereas the pattern BDAC reproduces better the \( \ell = 3 \) peak, it is the form DBCA for the \( \ell = 5 \) peak. The best result is achieved when both degenerate patterns are summed.

* Present address: Physics Department, University of Liverpool, Oliver Lodge Lab., Liverpool L69 7ZE, England

[1] M. Isobe and Y. Ueda J. Phys. Soc. Jpn. 65, 1178 (1996).
[2] T. Chatterji, et al., Solid State Commun. 108, 23 (1998).
[3] T. Yoshimura, et al., J. Phys. Soc. Jpn. 67, 744 (1998).
[4] T. Ohama, et al., Phys. Rev. B 59, 2929 (1999).
[5] H. Smolinski, et al., Phys. Rev. Lett. 80, 5164 (1998); A. Meetsma, et al., Acta Cryst. C 54, 1558 (1998); H.G. von Schnering, et al., Z. Kristallogr. 213, 246 (1998).
[6] J. Lüdecke, et al., Phys. Rev. Lett. 82, 3633 (1999).
[7] J.L. de Boer, et al., Phys. Rev. Lett. 84, 3962 (2000).
[8] M.V. Mostovoy, and D.I. Khomskii, Solid State Commun. 113, 159 (1998).
[9] M.J. Konstantinovic, et al., Sol. State Commun. 112, 397 (1999).
[10] Y. Fagot-Revurat, M. Mehring, and R.K. Kremer, Phys. Rev. Lett. 84, 4176 (2000).
[11] T. Ohama, et al., J. Phys. Soc. Jpn. 69, 2751 (2000).
[12] B. Grenier, et al., Phys. Rev. Lett. 86, 5966 (2001).
[13] H. Nakao, et al., Phys. Rev. Lett. 85, 4349 (2000); J.E. Lorenzo, et al., Phys. Rev. Lett. 86 (2001).
[14] J.-L. Hodeau, et al., Chem. Rev. B101, 1843 (2001), and references therein.
[15] Y. Murakami, et al., Phys. Rev. Lett. 80, 1932 (1998); ibid. 81, 582 (1999).
[16] All reflections are indexed according to \( Pmnm \) setting.
[17] S. Van Smaalen, et al., cond-mat/0108067.
[18] K. Ohwada, et al., Phys. Rev. Lett. 87, 086402-1 (2001)