

## On the low-temperature structure and magnetic behaviour of $\eta$ -Na<sub>1.286</sub>V<sub>2</sub>O<sub>5</sub>

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2004 J. Phys.: Condens. Matter 16 S629

(<http://iopscience.iop.org/0953-8984/16/11/009>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 27/05/2010 at 12:52

Please note that [terms and conditions apply](#).

# On the low-temperature structure and magnetic behaviour of $\eta$ -Na<sub>1.286</sub>V<sub>2</sub>O<sub>5</sub>

F Duc<sup>1</sup>, P Millet<sup>1</sup>, F Chabre<sup>2</sup>, A M Ghorayeb<sup>2</sup> and A Stepanov<sup>2</sup>

<sup>1</sup> Centre d'Elaboration de Matériaux et d'Etudes Structurales, UPR 8011, BP 94347, 29 rue Jeanne Marvig, 31055 Toulouse Cedex 4, France

<sup>2</sup> Laboratoire Matériaux et Microélectronique de Provence, CNRS UMR 6137, Case 142, Faculté des Sciences de St-Jérôme, Université d'Aix-Marseille III, 13397 Marseille Cedex 20, France

E-mail: fduc@cemes.fr

Received 7 January 2004

Published 4 March 2004

Online at [stacks.iop.org/JPhysCM/16/S629](http://stacks.iop.org/JPhysCM/16/S629) (DOI: 10.1088/0953-8984/16/11/009)

## Abstract

In this work, we report on low-temperature x-ray diffraction, electron-spin-resonance and magnetic-susceptibility measurements performed on  $\eta$ -Na<sub>1.286</sub>V<sub>2</sub>O<sub>5</sub>. We show that the low-temperature structure of this compound differs from that at room temperature mainly by the doubling of the unit cell in the *b* direction. The magnetic measurements give evidence for the opening of a spin gap which we discuss in conjunction with the low-temperature structure of this compound.

## 1. Introduction

During the last decade, a variety of vanadium oxides have been recognized as low-dimensional quantum spin systems with remarkable magnetic properties. In this context, the sodium–vanadium–oxygen phase diagram has been the subject of intense research. In particular, the detailed study of the V<sup>4+</sup>-rich zone of this diagram has led to the structural characterization of the vanadium oxide bronze  $\eta$ -Na<sub>1.286</sub>V<sub>2</sub>O<sub>5</sub> [1, 2] (also denoted by the stoichiometric formula Na<sub>9</sub>V<sub>14</sub>O<sub>35</sub>). Isobe *et al* [2] reported a spin-gap behaviour for this compound, but mentioned that its magnetic susceptibility curve could not be fitted by theoretical equations for spin-gap systems, and suggested that this compound could be a new type of low-dimensional system. The structure of  $\eta$ -Na<sub>1.286</sub>V<sub>2</sub>O<sub>5</sub> (space group *P2/c*) is built up of layers consisting of VO<sub>5</sub> square pyramids sharing edges and corners with their apical oxygens pointing up and down alternately to form double strings in the [100] direction. These double strings are isolated in the [001] direction via VO<sub>4</sub> tetrahedra and have a stair-like shape with a step every ten VO<sub>5</sub> square pyramids. Whangbo and Koo [3] proposed a tentative explanation for the spin-gap behaviour in terms of a fused chain of 10-node rings, using a spin-dimer analysis. However, recently, new superstructure reflections were observed below  $T_c = 100$  K at the reduced wavevector  $q_c = (0, \frac{1}{2}, 0)$  indicating the occurrence of a structural phase transition [4]. In the light of

these findings, we have decided to re-examine the low-temperature behaviour of this compound. Here, we present the first results obtained on the low-temperature structure of  $\eta\text{-Na}_{1.286}\text{V}_2\text{O}_5$  as determined from x-ray scattering data acquired at 15 K, as well as complementary magnetic susceptibility and electron spin resonance (ESR) measurements.

## 2. Single crystal x-ray diffraction study

The x-ray diffraction data were collected with an *Xcalibur CCD* diffractometer (*Oxford Diffraction*; 2001) using graphite monochromated Mo  $K\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation. The temperature was controlled using a helium gas cryostream cooler (*Helijet Oxford Cryosystems*; 2001). A needle-like single crystal with dimensions of  $0.890 \text{ mm} \times 0.140 \text{ mm} \times 0.118 \text{ mm}$  was selected for the measurement. As the additional reflections were very weak in comparison with the main ones, the determination of the lattice parameters at 15 K from a peak search over the measured raw images (standard diffractometer software *Crysalis RED* [5]) led to the monoclinic lattice  $a = 15.2006(8) \text{ \AA}$ ,  $b = 5.0001(3) \text{ \AA}$ ,  $c = 20.776(1) \text{ \AA}$ ,  $\beta = 109.128(6)^\circ$ . This is commonly noted as the basic-structure unit-cell since only the main reflections are used. In fact, the presence of additional reflections at  $\pm q_c$  results in the doubling of the unit cell in the  $b$  direction. The raw frames were reduced to Bragg intensities using the standard diffractometer software *Crysalis RED* [5]. The integrated intensities were corrected for Lorentz and polarization effects. Absorption was corrected analytically using the crystal shape and the indices of the faces determined by the program *Movie* [5]. The systematic absences of the main reflections are still consistent with the space group  $P2/c$ . Using the 4227 main reflections (3626 observed ones with  $I > 3\sigma(I)$ ), the basic structure refined in  $P2/c$  gave a good fit to the data with the final reliability factors  $R(\text{obs/all}) = 0.0387/0.0438$  and  $wR(\text{obs/all}) = 0.0728/0.0775$ . The average structure obtained was quite similar to the model determined at room temperature [1, 2], except for the atomic displacement parameters which were in accordance with low-temperature measurements. The V atoms at the site V7, which is located at the corner of the double string, exhibited however the most anisotropic displacement parameters with  $U^{22} > 5U^{11}$  and  $U^{22} > 2.5U^{33}$ . It is interesting to note that the vanadium on this site was in the partial oxidation state  $\text{V}^{4.5+}$  at room temperature. The O atoms at the oxygen apical site O7 showed very anisotropic displacement parameters with  $U^{22} > 1.75U^{11}$  and  $U^{22} > 2U^{33}$  as well.

The additional reflections do not introduce other systematic absences. The space group of the superstructure on the corresponding  $a \times 2b \times c$  supercell is then the same as at room temperature, namely  $P2/c$ . However, the translational symmetry of the  $b$  lattice spacing, which kept the crystal invariant at room temperature, is no longer a symmetry at low temperature. The structural phase transition of the  $\eta\text{-Na}_{1.286}\text{V}_2\text{O}_5$  compound is therefore characterized by a symmetry breaking, which is typical of a second-order transition. Direct refinement of the superstructure failed, because the parameters appeared to be too severely correlated. The solution to this problem is provided by the superspace description of the structure [6, 7]. Thus all the reflections observed on the collected frames were indexed with four integers  $hk\ell m$  according to the four-dimensional base [6, 7]

$$\mathbf{H} = h\mathbf{a}^* + kb^* + \ell\mathbf{c}^* + m\mathbf{q} \quad (1)$$

where  $\mathbf{a}^*$ ,  $\mathbf{b}^*$ ,  $\mathbf{c}^*$  are the reciprocal axes of the basic structure and  $\mathbf{q}$  ( $\mathbf{q} = \mathbf{q}_c$ ) is the modulation vector. Main reflections have  $m = 0$ . Analysis of the data using the four-integer indexing system shows that there are 5175 observed reflections (3626 main ones, and 1549 satellites ( $|m| = 1$ ) with  $I > 3\sigma(I)$ ).

The atomic positions  $x_i^\mu$  in a one-dimensionally modulated structure are given as the sum of an average position and a shift:

$$x_i^\mu = \bar{x}_i^\mu + u_i^\mu(\bar{x}_4) \quad (2)$$

$$\bar{x}_i^\mu = L_i + \bar{x}_i^{0\mu} \quad (3)$$

$$\bar{x}_4 = t_0 + \mathbf{q} \cdot \mathbf{x} \quad (4)$$

where  $\bar{x}_i^\mu$  ( $i = x, y, z$ ) are the coordinates of an atom  $\mu$  in the average structure,  $L_i$  are integers and  $\bar{x}_i^{0\mu}$  the average position within the unit cell. The components of the modulation function of atom  $\mu$  are  $u_i^\mu(\bar{x}_4)$  with  $u_i^\mu(\bar{x}_4 + 1) = u_i^\mu(\bar{x}_4)$ .  $\bar{x}_4 = t_0 + \mathbf{q} \cdot \mathbf{x}$  is the fourth superspace coordinate with starting phase  $t_0$ . Because of the commensurateness, the modulation functions are written as a finite Fourier expansion. Only the first-order harmonics were included in the refinement:

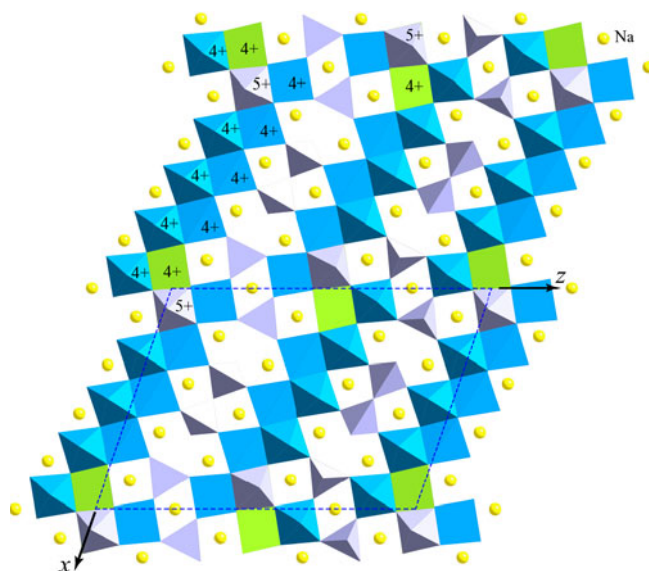
$$u_i^\mu(\bar{x}_4) = A_i \sin(2\pi \bar{x}_4) + B_i \cos(2\pi \bar{x}_4). \quad (5)$$

The symmetry of the modulated structure is described by the superspace group  $P2/c(0\beta 0)00$  [7, 8]. The average model was used as a starting point for the refinement of the modulated structure. 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 program *Jana2000* [9]. The value of the starting phase  $t_0$  defining the symmetry of the superstructure [10] has to be determined from the refinement. The best solution was obtained with  $t_0$  equal to  $\frac{1}{4}$  and with a simple harmonic displacement of all atoms. Thus the centres of symmetry located on (000) and  $(0\frac{1}{2}0)$  are lost in the supercell, and only those located on  $(0\frac{1}{4}0)$  and  $(0\frac{3}{4}0)$  remain. Only the components of the amplitude of the sine term were refined. The final refinement converged to  $R = 0.0451$  for all observed reflections ( $R = 0.0395$  for the main reflections and  $R = 0.1178$  for the satellite reflections).

Our refinement shows that V atoms at the site V7 and the corresponding apical oxygen O7 are the most displaced from their average position. Two Na atoms also contribute to the intensity of the satellite reflections, namely, the Na1 and Na5 sites, which are close to the V7 site. The other atoms remain almost fixed. The modulations mainly occur along the [010] direction, indicating the longitudinal mode of displacements. The two positions (noted  $a$  and  $b$ ) resulting from the modulations of these atoms in the corresponding  $a \times 2b \times c$  supercell are reported in table 1. The positions of the oxygen ions coordinated to V7 are also given.

The model obtained leads to V7–O7 bonds unchanged with respect to room temperature. This means that V7 and O7 move in phase along the [010] direction. On the other hand, as the other oxygen atoms are almost not displaced from their average position, two types of V–O basal plane pyramid changes in the first coordination sphere of V7 can be observed: an expansion (for V7a) and a contraction (for V7b). As the formal valence of V<sup>4.5+</sup> was assigned to the V7 site at room temperature, we attribute the formal valence state V<sup>4+</sup> to the expanded pyramid, and the oxidation state V<sup>5+</sup> to the contracted pyramid. This hypothesis was confirmed with the calculation of the valences of V sites using the bond-valence method [11]. The existence of two kinds of V7 sites results in an alternating charge ordering with the sequence 4+, 5+, 4+, 5+, . . . , along the  $b$  axis and in a peculiar charge ordering along the infinite double strings in the ( $a$ ,  $c$ ) planes. Indeed, on the ten VO<sub>5</sub> square pyramids along the double strings in the stair-like shape, nine V cations are in the oxidation state V<sup>4+</sup> and one, which is located at the corner of the double string, is in the V<sup>5+</sup> state (figure 1).

As mentioned earlier, the modulations are not restricted only to the V7 and O7 atom sites. The Na atoms close to the V7 atoms, i.e. the Na1 and Na5 sites, are also displaced along the [010]



**Figure 1.** A projection of the  $T = 15$  K  $\eta$ - $\text{Na}_{1.286}\text{V}_2\text{O}_5$  structure onto (010). The oxidation state (4+ or 5+) of each vanadium atom along the double strings is indicated. The dashed line is the unit cell.

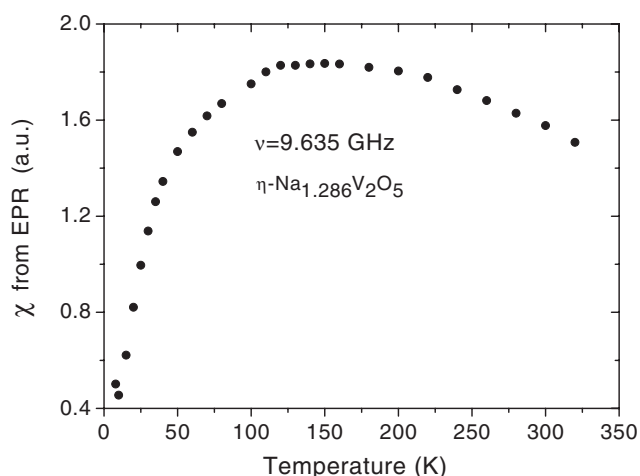
(This figure is in colour only in the electronic version)

**Table 1.** Positions resulting from the modulations of the most displaced atoms in the supercell.

Atom	$x$	$y$	$z$	$U_{\text{eq}} (\text{\AA}^2)$
V7a	0.906 14(4)	0.684 33(5)	0.476 87(3)	0.004 68(17)
V7b	0.908 03(4)	0.196 47(5)	0.478 69(3)	0.004 98(17)
Na1a	0	0.450 95(17)	0.75	0.007 0(6)
Na1b	0	0.947 47(17)	0.75	0.007 5(6)
Na5a	0.868 91(10)	0.430 22(13)	0.579 19(7)	0.008 9(4)
Na5b	0.871 23(9)	0.924 46(13)	0.577 75(7)	0.007 5(4)
O7a	0.900 13(15)	0.526 1(2)	0.487 61(11)	0.006 3(4)
O7b	0.904 65(16)	0.038 7(2)	0.489 97(12)	0.009 9(5)
O14a	0.162 19(15)	0.267 5(2)	0.617 03(11)	0.006 4(4)
O14b	0.162 30(15)	0.766 5(2)	0.616 17(11)	0.006 2(4)
O17a	0.797 38(15)	0.764 2(2)	0.490 95(11)	0.005 9(4)
O17b	0.799 08(15)	0.263 9(2)	0.490 44(11)	0.005 6(4)
O18a	0.011 73(14)	0.264 9(2)	0.943 24(11)	0.006 7(4)
O18b	0.005 09(14)	0.766 6(2)	0.942 16(11)	0.006 2(4)

direction with respect to their average position. However, their displacements are smaller than the ones observed for V7 and O7 ( $b \times \Delta y(\text{Na}1) \simeq \pm 0.075(1) \text{\AA}$ ,  $b \times \Delta y(\text{Na}5) \simeq \pm 0.150(1) \text{\AA}$ ,  $b \times \Delta y(\text{V}7/\text{O}7) \simeq \pm 0.300(1) \text{\AA}$ ).

These results show that the low-temperature phase of  $\text{Na}_{1.286}\text{V}_2\text{O}_5$  is characterized by a three-dimensional ordering of the  $\text{V}^{4+}/\text{V}^{5+}$  atoms on the V7 site, which corresponds to a charge ordering. The Na atoms, which ensure the balance of charges, are sensitive to this charge ordering.



**Figure 2.** The temperature dependence of the susceptibility of  $\eta$ - $\text{Na}_{1.286}\text{V}_2\text{O}_5$  as deduced from the double integration of the ESR signal.

### 3. Magnetic-susceptibility and electron-spin-resonance measurements

We have measured the magnetic susceptibility of  $\eta$ - $\text{Na}_{1.286}\text{V}_2\text{O}_5$  in a field of 1 T, between 1.8 and 330 K, using a *Quantum Design* SQUID magnetometer. The obtained susceptibility curve (not shown here) is similar to that reported by Isobe *et al* [2] in that it shows, in particular, a spin-gap behaviour at low temperature and a small kink, just above 100 K, which we attribute to the structural phase transition discussed above. In addition, we have performed an ESR spectroscopy study on this compound, between 4.2 and 330 K, using a *Bruker EMX* spectrometer operating in the X-band ( $\nu = 9.635$  GHz). We here show in figure 2 the susceptibility of  $\eta$ - $\text{Na}_{1.286}\text{V}_2\text{O}_5$  as deduced from the double integration of the ESR signal.

The temperature dependence of the spin susceptibility deduced from the ESR spectra is similar to that directly measured by the SQUID magnetometer. In the light of the structural data discussed above, the origin of the spin-gap behaviour may now be attributed to the fact that the magnetic unit cell contains, below 100 K, 18 spins instead of 9 as was the case at room temperature, due to the doubling of the  $b$  lattice parameter. A detailed study (which will be reported elsewhere) of the measured susceptibility has allowed us to suggest that the gap value is around 35 K.

### 4. Conclusion

From x-ray diffraction measurements performed at 15 K on single crystals of  $\eta$ - $\text{Na}_{1.286}\text{V}_2\text{O}_5$ , we report on the low-temperature structure of this compound and show that it differs from that at room temperature mainly by the doubling of the  $b$  lattice parameter. Magnetic-susceptibility and ESR measurements give evidence for a spin-gap behaviour, which we discuss in association with the low-temperature structure of this compound.

### Acknowledgments

The authors owe many thanks to the people involved in this work: S Ravy, A Thiollet, V A Pashchenko, J Y Henry and F Mila.

## References

- [1] Millet P, Henry J Y and Galy J 1999 *Acta Crystallogr. C* **55** 276
- [2] Isobe M, Ueda Y, Oka Y and Yao T 1999 *J. Solid State Chem.* **145** 361
- [3] Whangbo M H and Koo H J 2000 *Solid State Commun.* **115** 115
- [4] Ravy S 2001 private communication
- [5] Oxford Diffraction 2001 *XcaliburSystem, User Manual. CrysAlis Software Package. Version 1.167* Oxfordshire, UK
- [6] de Wolff P M 1974 *Acta Crystallogr. A* **30** 777
- [7] Janssen T, Janner A, Looijenga-Vos A and de Wolff P M 1993 *Mathematical, Physical and Chemical Tables (International Tables for Crystallography vol C)* ed A J C Wilson (New York: Kluwer–Academic) pp 797–835
- [8] Yamamoto A 1996 *Acta Crystallogr. A* **52** 509
- [9] Petříček V and Dušek M 2000 *Jana2000. Structure Determination Software Programs* (Praha, Czech Republic: Institute of Physics)
- [10] Dušek M 2002 private communication
- [11] Brown D and Altermatt D 1985 *Acta Crystallogr. B* **41**