

# $\tau$ - $\text{Na}_x\text{V}_2\text{O}_5$ ( $x = 0.64$ ): A Vanadium Bronze with an Original Intergrowth Structure

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The structure of the new vanadium oxide bronze VOB,  $\tau$ - $\text{Na}_{0.64}\text{V}_2\text{O}_5$ , exhibits an intergrowth structure built up by D4 and DZ layer types characteristic of  $\delta$ - $\text{Na}_x\text{V}_2\text{O}_5$  and the still unknown  $\zeta$ - $\text{M}_x\text{V}_2\text{O}_5$  VOB. The  $\tau$ - $\text{Na}_{0.64}\text{V}_2\text{O}_5$  phase, prepared at 650°C, crystallizes in the monoclinic system, space group  $C2/m$ , parameters  $a = 11.674(9)$  Å,  $b = 3.650(2)$  Å,  $c = 8.905(5)$ ,  $\beta = 91.04^\circ$ ,  $V = 379.65$  Å<sup>3</sup>,  $Z = 4$ . The sodium atoms intercalated between the layers favor the cohesion of the network and have the same type of coordination polyhedra between D4-D4 or D4-DZ interspace; this fact explains the original intergrowth structure. Sodium atoms have a different environment in the DZ-DZ interspace. Comparisons with the related structures  $\delta$ - $\text{M}_x\text{V}_2\text{O}_5$  ( $M = \text{Ag}, \text{Sr}, \text{Na}$ ),  $\rho$ - $\text{K}_{0.50}\text{V}_2\text{O}_5$ ,  $\nu$ - $\text{M}_x\text{V}_2\text{O}_5$  ( $M = \text{Ca}, \text{K}, \text{Rb}, \text{NH}_4$ ),  $\varepsilon$ - $\text{Cu}_x\text{V}_2\text{O}_5$ , are established and discussed. © 1996

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## INTRODUCTION

In a recent paper, one of us (J.G.) has proposed original structural relationships emerging from the detailed analysis of the  $\text{V}_2\text{O}_5$  layer structure. The possibilities of shearing and reorganizing explain the formation of simple ( $\alpha$ ,  $\varepsilon$ ,  $\delta$ ,  $\gamma$ , and  $\alpha'$ ) and double ( $\delta$ ,  $\nu$ ,  $\varepsilon$ , and  $\rho$ ) layer structures as well as the three-dimensional network of  $\beta$  and  $\beta'$  phases (1, 2).

In the wide family of the vanadium oxide bronzes (VOB), the  $(\text{V}_2\text{O}_5)_n$  double layers exhibit three architectural varieties known as D4, D4M, and DZ (D4 names  $(\text{V}_2\text{O}_5)_n$  double layers built up by endless quadruple chains of  $\text{VO}_6$  octahedra sharing edges of their equatorial plane and associated along the short  $b$  axis (i.e.,  $\approx 3.6$  Å) by edges, D4M being its mirror image; DZ depicts a  $(\text{V}_2\text{O}_5)_n$  layer obtained from a cross-linked double string of  $\text{VO}_6$  octahedra sharing edges and corners). The first is illustrated by  $\delta$ - $\text{Ag}_x\text{V}_2\text{O}_5$  (Andersson (3)), which is a prototype structure. In the  $\rho$ - $\text{K}_x\text{V}_2\text{O}_5$  VOB, D4 and D4M layers alternate as demonstrated by Savariault *et al.* (4), the potassium atoms leading to the network cohesion. Hitherto, a VOB built up with DZ layers has not been isolated.

In the  $\text{Na}_x\text{V}_2\text{O}_5$  system three phases have been characterized and their homogeneity range determined:

—the  $\alpha$  phase ( $0 \leq x \leq 0.02$ ) has an orthorhombic structure identical with the  $\text{V}_2\text{O}_5$  layer structure, doped Na atoms lying between the layers ( $Pm\bar{m}n$ ,  $a = 11.516$  Å,  $b = 3.565$  Å,  $c = 4.370$  Å for  $x = 0.02$ ) (2);

—the  $\beta$  phase with  $0.20 \leq x \leq 0.40$ , monoclinic, was originally isolated by Wadsley, who also determined its crystal structure ( $C2/m$ ,  $a = 15.44$  Å,  $b = 3.61$  Å,  $c = 10.08$  Å,  $\beta = 109.6^\circ$  for  $x = 0.33$ ) (5).

—the  $\alpha'$  phase with  $0.70 \leq x \leq 1$ .  $\alpha'$ - $\text{Na}_x\text{V}_2\text{O}_5$  crystallizes in the orthorhombic system. The structure derives from the  $\text{V}_2\text{O}_5$  one but possesses the noncentric space group  $P2_1mn$  ( $a = 11.318$  Å,  $b = 3.611$  Å,  $c = 4.797$  Å for  $x = 1$ ). The structure was determined and refined by Galy *et al.* (6, 7).

More recently another bronze,  $\text{Na}_{0.56}\text{V}_2\text{O}_5$  (monoclinic,  $C2/m$ ,  $a = 11.663$  Å,  $b = 3.6532$  Å,  $c = 8.92$  Å,  $\beta = 90.91^\circ$ ), was prepared by Kanke *et al.* (8) as single crystals by chemical transport, using HCl gas as transport medium, from a mixture of  $\text{NaVO}_3$ ,  $\text{V}_2\text{O}_4$ , and  $\text{V}_2\text{O}_5$  at 923 K. This phase, according to our classification, contains D4 layers and should be designated  $\delta$ - $\text{Na}_{0.56}\text{V}_2\text{O}_5$ .

While studying sodium vanadium bronzes and more particularly the  $\alpha'$ - $\text{Na}_x\text{V}_2\text{O}_5$  phases for copper exchange in the perspective of catalytic experiments (9), a new phase was obtained as single crystals during the synthesis: it was called  $\tau$ - $\text{Na}_x\text{V}_2\text{O}_5$  (10). The synthesis and crystal structure investigation of this original  $\tau$  phase is the subject of the present paper.

## EXPERIMENTAL SECTION

The synthesis procedures for  $\text{Na}_x\text{V}_2\text{O}_5$  VOB have been described in detail in a previous paper (11). We recall here the conditions in which the  $\tau$  phase is obtained.

A well-ground mixture of the appropriate amounts of  $\text{Na}_2\text{C}_2\text{O}_4$  and  $\text{V}_2\text{O}_5$ ,  $\text{Na:2V} = 0.70$ , were placed in a gold crucible and introduced in a quartz tube under a controlled atmosphere. The conditions were the following:  $\text{N}_2$  atmo-

sphere or vacuum; temperature increases at 3°C/mn heating rate; stabilized temperature at ca. 650°C for three days; cooling, down to room temperature, within four hours.

Small blue-black single crystals, with a prismatic shape, were selected from the crystals contained in the crucible. The X-ray powder pattern revealed unknown diffraction peaks, unindexed with the  $\alpha'$ - $\text{Na}_x\text{V}_2\text{O}_5$  cell parameters. The specific mass was deduced from a flotation experiment realized in diiodomethane the crystals behaving roughly like a Cartesian diver.

All the technical data concerning the registration measurements as well as structural refinement parameters are summarized in Table 1.

## CRYSTALLOGRAPHIC STUDY

### Structure Determination

A preliminary radiocrystallographic study by Laue and Weissenberg techniques revealed that the  $\tau$  phase crystallizes in the monoclinic system, possible space groups are  $C2/m$ ,  $Cm$  or  $C2$ . With the aid of a CAD4 Enraf Nonius automatic diffractometer, the cell parameters were determined and refined after the centring of 25  $hkl$  reflections (see Table 1). The intensity of the  $hkl$  reflections were then measured; from a statistical study of the variance versus parity group, the centrosymmetric space group  $C2/m$  was clearly favored. Each intensity measurement was corrected for Lorentz and polarization factors.

Atomic scattering factors with their anomalous dispersion coefficients are those given by Cromer and Waber (12). The calculations using SHELX-86 (13) and drawings with ORTEP (14) were performed on the minisupercomputer ALLIANT VFX 80 of the laboratory.

The structure was determined through Patterson function deconvolution, Fourier and difference Fourier synthesis. The cell parameters are very similar to those of the  $\delta$ - $\text{Na}_{0.56}\text{V}_2\text{O}_5$  VOB (8). From the identical distribution of the  $hkl$  intensity revealed by the  $h0l$  and  $h2l$  Weissenberg diagrams, it was clear that all the atoms were lying in the mirror planes  $y = 0$  and  $y = 1/2$ . It was hence surprising that only four atoms could be determined from the Patterson function, one vanadium, V1, and three oxygens, O1, O2, and O3. Subsequent Fourier synthesis followed by least-square refinement revealed two crystallographic sites occupied at 50% for V2 and also for O4 and O5, i.e., V2', O4', and O5'. All these crystallographic sites were condensed along an infinite  $(\text{V}_2\text{O}_5)_n$  double layer parallel to the (001) plane. Finally the presence of sodium atoms was detected between these layers. They occupy two distinct sites, Na1 and Na2.

The calculations gave a high reliability index  $R = 0.17$ . After absorption and secondary extinction correction, it was possible to reduce the  $R$  factor to 8%, all the atoms being refined with anisotropic thermal parameters. Owing

TABLE 1  
Physical Properties and Parameters Pertinent to Data Collection and Refinement of  $\tau$ - $\text{Na}_x\text{V}_2\text{O}_5$

Physical properties	
Formula	$\text{Na}_{0.64}\text{V}_2\text{O}_5$
Mol. wt. (g)	197.052
Cryst. system	Monoclinic
Space group	$C2/m$
$a$ (Å)	11.674(9)
$b$ (Å)	3.650(2)
$c$ (Å)	8.905(5)
$\beta$ (°)	91.04(4)
$V$ (Å <sup>3</sup> )	379.65
$Z$	4
$F000$	373
$\rho_{\text{exp.}}$ (g/cm <sup>3</sup> )	3.3(1)
$\rho_{\text{calc.}}$ (g/cm <sup>3</sup> )	3.4
Crystal shape	black prism
Faces	{001}, {100}, {010}
Distances to center (cm)	0.0012, 0.0068, 0.0324
Parameters of data collection and refinement measurements	
Temperature (K)	293
$\lambda$ (Å)	0.71073
Take off (°)	6.0
Detector width (mm)	4 × 4
Scan type	$\omega/2\theta$
Scan width (°)	1.00 + 0.40 tan $\theta$
$hkl$ range	$h$ 0 → 23, $k$ 0 → 7, $l$ -17 → 17
$\theta$ range (°)	1 → 45
No. of measured reflections (with $h + k = 2n$ )	1850
Standards (period)	
Intensity (1 hr)	{006}, {600}, {020}
Orientation (100 reflections)	{-600}, {0-20}, {0-23}
Absorption correction	
$\mu(\text{MoK}\alpha)$ (cm <sup>-1</sup> )	47.8
Gaussian grid	4, 8, 32
Transmission factor	0.64-0.91
Averaging	
$R_{\text{av}} = \Sigma(I - I_{\text{av}})/(\Sigma I)$	0.048
Refinements	
No. of variables (NV)	74
No. of unique reflections with $I \geq 3 \sigma(I)$ (NO)	1721
Weighting scheme	$w = 0.94/[\sigma^2(I) + 0.005 \times F_0^2]^{1/2}$
Maximum shift (e.s.d.)	0.02
Agreement factors	
$R = (\Sigma  F_0  -  F_c  )/(\Sigma F_0 )$	0.085
$Rw = [\Sigma( F_0  -  F_c )^2 / (\Sigma F_0 ^2)]^{1/2}$	0.089
$s = [\Sigma( F_0  -  F_c )^2 / (\text{NO} - \text{NV})]^{1/2}$	1.164

to the poor quality of the crystal (in spite of a selection among six single crystals investigated) and the partial disorder obviously affecting the  $(\text{V}_2\text{O}_5)_n$  layers, it was decided to keep this average structure and to attempt to understand its outward complexity.

Atomic fractional coordinates, equivalent isotropic ther-

TABLE 2  
Final Least-Squares Atomic Parameters with Estimated  
Standard Deviations for  $\tau$ -Na<sub>x</sub>V<sub>2</sub>O<sub>5</sub>

Atom	$t^*$	$x$	$y$	$z$	$B_{\text{eq}}$ (Å)
V1	1	0.0844(2)	0	0.1659(3)	0.55(5)
V2	0.5	0.3832(6)	0	0.1637(9)	2.9(2)
V2'	0.5	0.2105(5)	0	0.8352(8)	2.9(2)
O1	1	-0.079(1)	0	0.102(1)	2.4(3)
O2	1	0.087(1)	0	0.346(1)	2.5(3)
O3	1	0.241(1)	0	0.118(2)	2.6(3)
O4	0.5	0.551(1)	0	0.144(2)	1.2(4)
O4'	0.5	0.391(2)	0	0.866(2)	1.6(4)
O5	0.5	0.360(2)	0	0.350(2)	2.5(5)
O5'	0.5	0.190(2)	0	0.647(2)	2.5(4)
Na1	0.28(1)	0.284(3)	0	0.521(4)	4.3(5)
Na2	0.36(1)	0.462(2)	0	0.484(3)	2.9(5)

Note.  $t^*$  = occupancy factor;  $B_{\text{eq}} = 8\pi^{2/3}$  trace  $u(u)$ , diagonalized  $U$  matrix).

mal parameters (Å<sup>2</sup>), and occupancy factors are given in Table 2 and the main interatomic distances (Å) in Table 3. Anisotropic thermal parameters and structure factors can be supplied on request.

### Structure Description

The various atomic sites projected onto the (010) plane are represented in Fig. 1a. A careful analysis of the vana-

dium and oxygen distributions indicates two unique solutions leading to two distinct crystal structures:

—a phase, built up from V1, V2, O1, O2, O3, O4, and O5 atoms, named  $\zeta$ -Na<sub>x</sub>V<sub>2</sub>O<sub>5</sub> (Fig. 1b);

—the  $\delta$ -Na<sub>x</sub>V<sub>2</sub>O<sub>5</sub> phase, organized again around V1, O1, O2, and O3 but with V2', O4', and O5' (Fig. 1c).

In both cases the sodium atoms held together the (V<sub>2</sub>O<sub>5</sub>)<sub>n</sub> layers. The single crystal studied appears to be an extremely original case of a perfect intergrowth of two crystal structures, both of which are detailed below.

$\zeta$ -Na<sub>x</sub>V<sub>2</sub>O<sub>5</sub>. In this structure (Fig. 1b) two cross-linked infinite chains of distorted VO<sub>6</sub> octahedra develop along the [010] direction associated at the same level by edge sharing, two [V1O<sub>6</sub>] via O1–O1c and two [V2O<sub>6</sub>] via O4–O4b. These double strings are held together by corner sharing, O3 and O3b, forming an infinite (V<sub>2</sub>O<sub>5</sub>)<sub>n</sub> layer parallel to the (001) plane. The chemical bonding shows large differences in the vanadium–oxygen distances. The short V1–O2 and V2–O5 bond points to the border of the (V<sub>2</sub>O<sub>5</sub>)<sub>n</sub> layer; the bonds directed through the median plane are very long, V1–O1c and V2–O4b, implying a certain weakness. This fact has been already noted by one of us (J.G. (2)) in the demonstration of the formation of such layers, named DZ, from the typical simple layer of the vanadium pentoxide V<sub>2</sub>O<sub>5</sub> crystal structure refined by Enjalbert *et al.* (15).

The first sodium crystallographic site Na1 is enclosed in a distorted trigonal prism O5bO2b O5O2O5bO2b, the pseudo-threefold axis of which is aligned in the [100] direction. These [Na1O<sub>6</sub>] polyhedra sharing faces along [010] develop a kind of tunnel with a parallelogram section. Na1 and Na1b sites are occupied at 50% maximum owing to their proximity, Na1 – Na2 = 2.12(3) Å. Twinned Na2 sites (Na2, Na2c), being very close to a symmetry center and therefore half-occupied, are surrounded by six oxygen atoms making an octahedron (Na2,Na2c)O5(O2bO2a)<sub>2</sub>O5c. In fact Na2 is moved toward an apex of the octahedron, i.e., O5, defining a Na2(O2aO2b)<sub>2</sub>O5 square pyramid. Such a coordination for Na is not common. We encountered it once before in the original cubic pseudo-zeolitic network of a copper(II)-uridine complex (16). Like Kanke *et al.* (8) we believe that, when the Na2 site is occupied, there is a local distortion in order to accommodate it. Such a phenomenon must occur as well as in the succession of  $\zeta$ - $\zeta$ ,  $\delta$ - $\delta$ , or  $\delta$ - $\zeta$  layers.

$\delta$ -Na<sub>x</sub>V<sub>2</sub>O<sub>5</sub>. Four VO<sub>6</sub> octahedra are associated at the same level by three common edges making infinite quadruple strings along [010]; associated by edges with identical quadruple strings slipped by  $b/2$ , they form (V<sub>2</sub>O<sub>5</sub>)<sub>n</sub> double layers. In these layers, long bond distances crossing the median plane again occur (dotted lines in Fig. 1c).

The polyhedra around Na1 and Na2 are quite different from those of the  $\zeta$  phase. Na1 sites repeated by a twofold

TABLE 3  
Selected Interatomic or Inter-site (\*) Distances (Å)  
for  $\tau$ -Na<sub>x</sub>V<sub>2</sub>O<sub>5</sub>

V1 – O2 1.61(1)	*Na1 – Na1b 2.02(2)	*Na1 – Na2 2.12(3)
V1 – O1 1.98(1)	*Na2 – Na2c 0.92(2)	Na2c – Na1a 4.18(3)
V1 – O3 1.89(1)	Na1 – Na2b 3.40(3)	Na2b – Na1b 2.96(3)
2 × V1 – O4a 1.876(4)		
2 × V1 – O4'b 1.872(5)		
V1 – O1c 2.39(1)		
$\zeta$ FORM		
V2 – O5 1.68(2)	Na1 – O2 2.75(3)	*Na2 – O5 1.67(3)
V2 – O3 1.70(1)	*Na1 – O5 1.78(4)	2 × Na2 – O2a 2.65(2)
V3 – O4 1.98(2)	2 × Na1 – O2b 2.63(2)	2 × Na2 – O2b 2.45(2)
2 × V2 – O1a 1.958(5)	2 × Na1 – O5b 2.75(3)	Na2 – O5c 2.53(3)
V2 – O4b 2.86(2)		
	V1a – V1b 3.522(5)	V1a – V2 2.976(6)
	V2 – V2c 4.030(9)	V1a – V2c 3.488(8)
$\delta$ FORM		
V2' – O5' 1.69(2)	*Na1 – O5' 1.58(4)	2 × Na2 – O2a 2.65(2)
V2' – O1d 1.64(1)	Na1 – O2 2.75(3)	2 × Na2 – O2b 2.45(2)
V2' – O4' 2.12(2)	2 × Na1 – O2b 2.63(2)	2 × Na2 – O5'b 2.79(2)
2 × V2' – O3b 1.955(5)	2 × Na1 – O5'b 2.38(2)	
V2' – O3e 2.53(2)		
	V1 – V2'f 3.316(7)	V1a – V1b 3.522(5)
	V1 – V2'b 3.012(5)	

Note. (a)  $-1/2 + x, \pm 1/2 + y, z$ ; (b)  $1/2 - x, \pm 1/2 - y, 1 - z$ ; (c)  $1 - x, \pm 1 - y, 1 - z$ , (d)  $-x, -y, 1 - z$ ; (e)  $x, y, 1 + z$ ; (f)  $x, y, -1 + z$ .

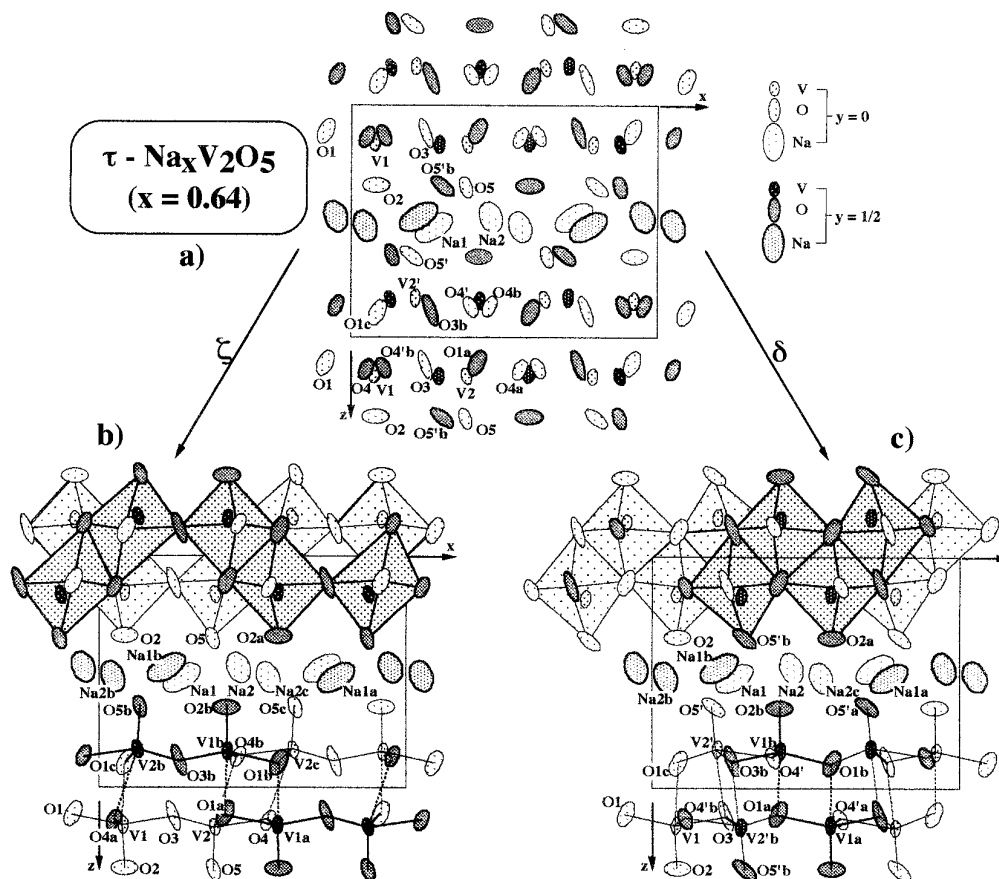


FIG. 1. Projection onto the (010) plane of the  $\tau$ - $\text{Na}_x\text{V}_2\text{O}_5$  structure. (a) projection of all the crystallographic sites occupied by Na, V, and O atoms; (b) first selection (V1, O1, O2, O3, V2, O4, O5) conducing to the  $\zeta$ - $\text{Na}_x\text{V}_2\text{O}_5$  form; (c) the  $\delta$ - $\text{Na}_x\text{V}_2\text{O}_5$  form obtained with the second set of atoms (V1, O1, O2, O3, V2', O4', O5').

axis in Na1b are occupied at 50% maximum. Na1 is again in a distorted trigonal prism O2bO5'bO2O5'O2bO5'b, its pseudo-trigonal axis being aligned roughly in [102] direction. Na2 and Na2c sites occupied at 50% are in an oxygenated rhombic prism (two trigonal prisms associated by a rectangular face (O2bO2a)<sub>2</sub>). The (Na<sub>2</sub>O<sub>6</sub>) polyhedron is rather regular; they share triangular faces and develop tunnels along [010] direction. Here again there are surely local constraints when sodium sites are occupied.

## DISCUSSION AND CONCLUSION

The  $\tau$ - $\text{Na}_x\text{V}_2\text{O}_5$  phase is an intergrowth of both  $\zeta$ - and  $\delta$ - $\text{Na}_x\text{V}_2\text{O}_5$  structures. The difficulty of obtaining good single crystals, reasonably linked to the intergrowth phenomenon, explains the rather high temperature factors found for the various atoms and the modest reliability index (classically the  $B$  ( $\text{\AA}^2$ ) factors, respectively, for vanadium, oxygen, and sodium atoms are between 0.4–0.6, 0.8–1.2, and 2–2.5). Nevertheless, this  $\tau$ - $\text{Na}_x\text{V}_2\text{O}_5$  average structure is clearly consistent.

The  $\delta$ -phase was first investigated by Andersson with silver atoms between the (V<sub>2</sub>O<sub>5</sub>)<sub>n</sub> layers (3). In the  $\tau$ -phase, the  $\delta$  part is very similar to the isolated  $\delta$ - $\text{Na}_{0.56}\text{V}_2\text{O}_5$  phase of Kanke *et al.* (8). The first point concerns the chemistry of these phases and more particularly their stoichiometry. It is obvious that new ways of chemical synthesis open new possibilities for obtaining such phases and explain why we must add these phases to the previous ones  $\alpha$ ,  $\beta$ , and  $\alpha'$  resulting from direct solid state synthesis. Kanke *et al.* underlined that their sites for sodium atoms (only one crystallographic site has been found) are too close and they should be half occupied. The result would be a maximum of 0.5 for  $x$ ,  $\text{Na}_{0.50}\text{V}_2\text{O}_5$ . To explain the  $x = 0.56$  value, they suggest that, when two of these near-sodium sites are occupied the atoms are repelled; they could explain the large anisotropic thermal parameters. We have already noted that such large thermal parameters are classically found in such structures. In our case, two sites were found, with different oxygen coordination polyhedra, which explains why  $x$  could increase to the maximum value of 1. Supposing the Na2a site to be occupied, then the next possible site

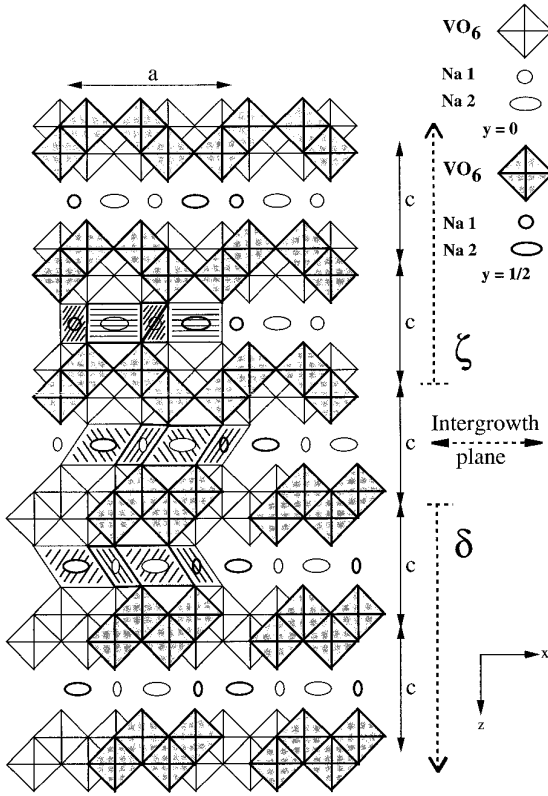


FIG. 2. Idealized drawing of the structure showing that in the intergrowth plane (between D4-DZ layers) the oxygen coordination polyhedra around the Na atoms are the same as those in between the D4-D4 layers of the  $\delta$ -Na<sub>x</sub>V<sub>2</sub>O<sub>5</sub> form.

occupancy is Na1 (Na2a – Na1 = 2,96(3) Å) (Na1b must be skipped, being too close Na2a – Na1b = 2.12(4) Å). The next site becomes Na2c (Na1 – Na2c = 2.96(3) Å) and then Na1a. All these sodium sites have reasonable oxygen polyhedra, while distorted, in both  $\zeta$ - and  $\delta$ -Na<sub>x</sub>V<sub>2</sub>O<sub>5</sub> touching Na–O, indicated by an asterisk in Table 3, are not plausible; such a distorted indication can be reasonably linked to the fact that the final result gives an average structure.

TABLE 4  
Volumes of VO<sub>6</sub> Octahedra and Valency of the Central Vanadium Atoms

Layer	Atoms	Volume (Å <sup>3</sup> )	Valency
$\zeta$	V1 (O2, 2 × O4a, O3, O1, O1c)	9.10	4.8(2)
	V2 (O5, O3, 2 × O1d, O4, O4e)	9.83	4.5(2)
$\delta$	V1 (O2, 2 × O4'b, O3, O1, O1c)	9.10	4.8(2)
	V2' (O5', O1d, 2 × O3b, O4', O3e)	9.38	4.7(2)

The  $\tau$  phase intergrowth has an average concentration close to  $x = 0.64$ . Up to now, a pure  $\zeta$ -Na<sub>x</sub>V<sub>2</sub>O<sub>5</sub> phase has not been isolated. It is a forthcoming challenge.

This  $\tau$  phase, idealized in Fig. 2, with a succession of  $\zeta$  and  $\delta$  crystal structures, allows us to understand why this intergrowth is easy to make. If the Na atoms are in different polyhedra in  $\delta$  and  $\zeta$  phase between typical D4- and DZ (V<sub>2</sub>O<sub>5</sub>)<sub>n</sub>-type layers, it is noteworthy that, when sodium atoms are in the interlayer D4 – DZ, their oxygenated rhombic and trigonal prisms are mirror images of those existing between two homologous layers D4-D4 ( $\delta$  phase). It is to be noted that the thickness of both  $\delta$  or  $\zeta$  slabs built up with some (V<sub>2</sub>O<sub>5</sub>)<sub>n</sub> layers have no reasons to be definite; so their random sequence should not give any superstructure. Long exposure films do not exhibit any extra spots in the reciprocal lattice confirming these assertions.

This  $\tau$  phase structure by its original structural organization lends support to the proposed models for the formation of the double layers D4, D4M, and DZ (2).

The vanadium in both oxydation states V and IV tends to be fivefold coordinated in these phases. The calculated volumes of the distorted VO<sub>6</sub> octahedra of V1, V2, and V2' indicate that V1O<sub>6</sub> is slightly smaller than the remaining ones. Empirical calculations based on the suggestions of Brown *et al.* (17), Walthersson (18), and Altermatt *et al.* (19), show a higher valency on the V1 site, i.e., more V<sup>5+</sup> on this site than on V2 and V2' (see Table 4). Both remarks on volume and valency are in agreement. It is

TABLE 5  
 $\tau$ -Phase Crystallographic Data Comparison with  $\delta$ - and  $\rho$ -M<sub>x</sub>V<sub>2</sub>O<sub>5</sub> Vanadium Oxide Bronzes

Compounds M <sub>x</sub> V <sub>2</sub> O <sub>5</sub>	$x$	$a$ (Å)	$b$ (Å)	$c$ (Å)	$\beta$ (°)	$V$ (Å <sup>3</sup> )	$Z$	$V/Z$ (Å <sup>3</sup> )	Space group	References
$\tau$ -Na <sub>x</sub> V <sub>2</sub> O <sub>5</sub>	0.64	11.648(2)	3.650(7)	8.879(1)	90.9(1)	377.4	4	94.4	$C2/m$	Present work
$\zeta$ -Na <sub>x</sub> V <sub>2</sub> O <sub>5</sub> (?)	~0.50	~11.65	~3.66	~8.88	~91	~380	4	~95	$C2/m$	Extrapolated
$\delta$ -Ag <sub>x</sub> V <sub>2</sub> O <sub>5</sub>	0.68	11.742(8)	3.667(3)	8.738(5)	90.5(1)	376.2	4	94.1	$C2/m$	(3)
$\delta$ -Na <sub>x</sub> V <sub>2</sub> O <sub>5</sub>	0.56	11.663(9)	3.6532(7)	8.92(1)	90.91(4)	379.9	4	95.0	$C2/m$	(8)
$\delta$ -Sr <sub>x</sub> V <sub>2</sub> O <sub>5</sub>	0.50	11.759(8)	3.695(3)	8.789(5)	91.8(1)	381.9	4	95.5	$C2/m$	(20)
$\rho$ -K <sub>x</sub> V <sub>2</sub> O <sub>5</sub>	0.50	11.607(3)	3.674(1)	18.670(8)		796.2	8	99.5	$Ccmm$	(4)

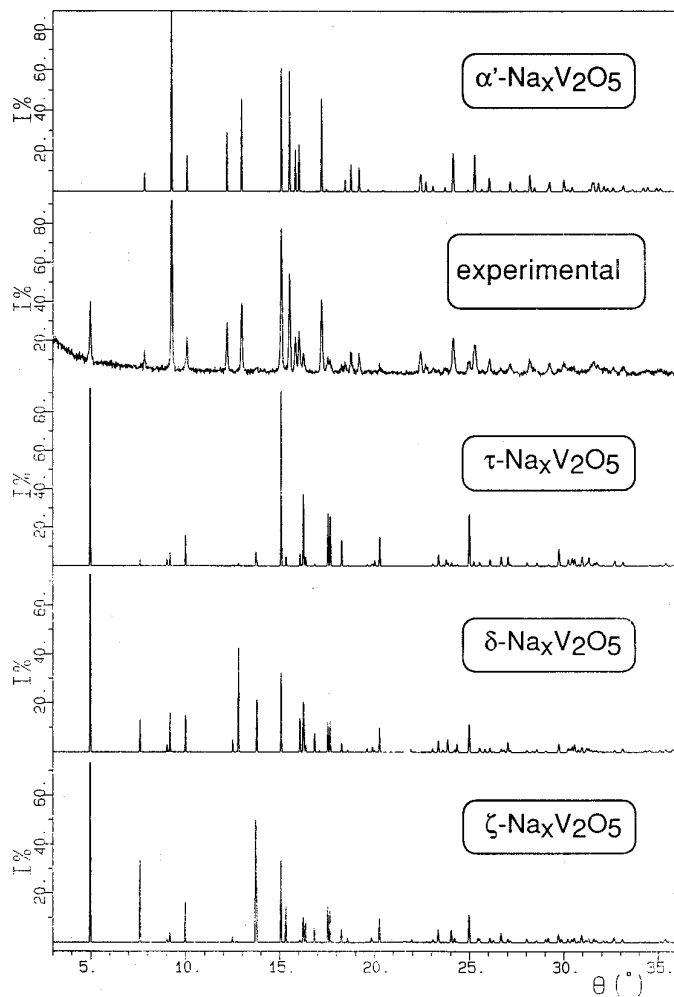


FIG. 3. Experimental XRD powder pattern of the bulk compared with the calculated ones for the components  $\tau$ - $\text{Na}_{0.64}\text{V}_2\text{O}_5$  and  $\alpha'$ - $\text{Na}_{0.70}\text{V}_2\text{O}_5$ . Simulated XRD of the  $\tau$ -,  $\delta$ -, and  $\zeta$ - $\text{Na}_x\text{V}_2\text{O}_5$  phases from the atomic coordinates of the  $\tau$  phase ( $\text{CuK}\alpha$ ).

reasonable to consider that in this structure there is no strong electronic localization as for  $\alpha'$ - $\text{Na}_x\text{V}_2\text{O}_5$  (6, 7). The double-bond character of the vanadyl group directed toward the sodium layer is strongly established for all the vanadium atoms, average  $\text{V}=\text{O} = 1.66 \text{ \AA}$ ; we again note also rather short bonds in the equatorial plane of the  $\text{V}_2\text{O}_6$  and  $\text{V}_2'\text{O}_6$  octahedra,  $\text{V}_2-\text{O}_3 = 1.70 \text{ \AA}$  and  $\text{V}_2'-\text{O}1f = 1.64 \text{ \AA}$  (this could be due to the average resolution of the structure). The sixth long bonds are more spread out, from 2.39 to 2.86  $\text{ \AA}$ .

New synthetic routes are now being explored to try to produce greater quantities of the  $\tau$ - $\text{Na}_x\text{V}_2\text{O}_5$  phase as well as of  $\delta$ - or  $\zeta$ - $\text{Na}_x\text{V}_2\text{O}_5$ . The data, more precisely the  $a$  and  $b$  parameters of the possible  $\zeta$ - $\text{Na}_x\text{V}_2\text{O}_5$  extracted from those of the  $\tau$  structure, can be compared with other  $\delta$ -phases, such as  $\delta$ - $\text{Sr}_x\text{V}_2\text{O}_5$  (20) or  $\rho$ - $\text{K}_x\text{V}_2\text{O}_5$ , having Andersson's  $\delta$ - $\text{Ag}_x\text{V}_2\text{O}_5$  as prototype structure (4) (Table 5). They also compare well with those of the  $\nu$ - $M_x\text{V}_2\text{O}_5$  ( $M = \text{Ca}, \text{K}, \text{Rb}, \text{NH}_4$ ) or  $\varepsilon$ - $\text{Cu}_x\text{V}_2\text{O}_5$  vanadium bronzes (2). Finally, the powder patterns of the  $\alpha'$ -,  $\tau$ -,  $\delta$ -, and  $\zeta$ - $\text{Na}_x\text{V}_2\text{O}_5$  phases calculated on the basis of the atomic positions provided are shown in Fig. 3. The experimental powder pattern realized after the crystallization shows the presence of both  $\alpha'$  and  $\zeta$  phases. They demonstrate that, in spite of their identical cell parameters and space group, the three phases,  $\tau$ ,  $\delta$ , and  $\zeta$ , could be identified by a careful analysis of the intensity of the first peaks. Such a calculation also provides a model from which the  $\zeta$  phase can be recognized in attempts to isolate it.

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