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A Proposal for (B) $VO_2 \Rightarrow$ (A) VO_2 Phase Transition: A Simple Crystallographic Slip

Jean Galy

Institut für Anorganische Chemie, Universität Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen, Germany; and Centre d'Elaboration de Matériaux et d'Etudes Structurales, Centre National de la Recherche Scientifique, 29, rue Jeanne Marvig, BP 4347, 31055 Toulouse Cedex, France

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(B) VO_2 crystallizes in the monoclinic system, $C2/m$ space group with $a = 12.093(1)$ Å, $b = 3.7021(2)$ Å, $c = 6.4330(5)$ Å, and $\beta = 106.97(1^\circ)$ as cell parameters. (A) VO_2 with two allotropic varieties crystallizes in the tetragonal system, the low temperature form A_L adopts $P4/ncc$ space group with $a = 8.4403(9)$ Å and $c = 7.666(1)$ Å and A_H the space group $I4/m$ with $a = 8.476(2)$ Å and $c = 3.824(2)$ Å. In these structures, VO_6 octahedra are associated in quadruple strings by edge sharing in the former structure whereas they form cross-linked double strings in the latter; both endless string types develop along parameters b or c (~ 3.8 Å periodicity). In the first association they build the so-called double layers D4 in (B) VO_2 and Dz in (A) VO_2, parallel to (001) and (110) planes, respectively, and associated, in their perpendicular direction, by corner sharing. These D4 layers exhibit the weakest V–O bonding perpendicular to their medium plane (parallel to (001)) allowing a crystallographic slip $Cs-1/3$ [100] (001) to occur in the structure, transforming (B) VO_2 into (A) VO_2. Design of (B) and (A) crystal structures via crystallographic shear mechanisms is related to chemical experimental conditions of formation: temperature, pressure, and stress. © 1999 Academic Press

INTRODUCTION

Vanadium dioxide exhibits a number of polymorphic forms: monoclinic (M1) VO_2 (1), which is stable at room temperature, prepared by solid state synthesis at 800°C from V_2O_5 and V_2O_3 mixtures; (M1) transforms at 68°C a tetragonal rutile form (R) VO_2 (2). In 1976, using soft chemistry routes, Théobald *et al.* made a pioneering work by discovering and characterizing two new varieties: (A) VO_2 and (B) VO_2 (3, 4). These authors showed that (A) crystallizes in the tetragonal system whereas (B) adopts the monoclinic system, space group $C2/m$, and a crystal structure isotypic with $Na_{0.20}TiO_2$ (5). All structural data were obtained by X-ray powder pattern indexing. The cell parameters are listed in Table 1. In 1993, Oka *et al.* showed by Rietveldt refinement of the (B) VO_2 structure that V^{4+}–V^{4+} pairing occurs with a subsequent magnetic susceptibility decrease when the phase cools down to 180 K (6).

These authors (7) also determined the (A) VO_2 crystal structure by Rietveldt analysis with a cell derived from that of Theobald, $a_{\text{new}} = a_{\text{old}}/\sqrt{2}$ and $c_{\text{new}} = c_{\text{old}}$, the space group being $P4_2/\text{ncm}$ (see Table 1). (A) VO_2 is isostructural with $CoMoO_4$ (8). They reported a reversible phase transformation at 162°C, parameter c being divided by 2 in the high temperature phase. They proposed a mechanism for the (A_L) $VO_2 \Rightarrow$ (A_H) VO_2 transformation associated with "detilting" of the VO_6 octahedra along the c-axis. However, they were not able to fully confirm this in a structural study performed at 200°C, the structure remaining the same with a slight variation of the V–V interatomic distances (9). Subsequently they mechanochemically induced the (B) $VO_2 \Rightarrow$ (A) VO_2 transformation by compressing or grinding, proposing a mechanism for this phase transition based on oxygen vacanices and vanadium atom shifts (10). A similar mechanism was proposed with a theoretical approach by Leroux *et al.* (11, 12). While writing the final version of this paper, Oka *et al.* published an X-ray single crystal structure refinement of the A_L and A_H VO_2 forms (13) (Table 1). A_L VO_2 variety is described in a different space group, $P4/ncc$, rather than $P4_2/ncm$, and A_H VO_2, with its half-parameter c (3.824 Å), adopting the $I4/m$ space group. For the purpose of our work the general description of both structures remains the same.

The aim of this paper is to propose another structural mechanism for (B) $VO_2 \Rightarrow$ (A) VO_2 phase transition and by providing structural description of these phases, derived from the basic V_2O_5, to try to correlate their formation to the chemical routes of synthesis: reduction, hydrothermal reactions, mechanochemical stress.

FORMATION OF (B) VO_2 AND (A) VO_2

The basic compound is vanadium pentoxide V_2O_5, with a layer structure in which vanadium coordination is purely square pyramidal (VO_5 SP). The single $[V_2O_5]_n$ layer,

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TABLE 1
Crystallographic Data

Phases	Phase transition	Cryst. system[a]	Space group	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)	d_{exp}	d_x	Z	Ref.
V_2O_5		ortho.	$Pmmn$	11.512	3.564	4.368		179.2		3.37	2	11
(R)Nb_2O_5		mon.	$C2/m$	12.79	3.826	3.983	90.8	194.9		4.53	2	17
(M1) VO_2	68°C	mon.	$P2_1/c$	5.743	4.517	5.375	122.61	117.5	4.65	4.69	4	1
(R) VO_2	68°C	tetrag.	$P4_2/mnm$	4.530	4.530	2.869		58.9		4.68	2	2
(B) VO_2	220°C	mon.	$C2/m$	12.03	3.693	6.420	106.6	273.3		4.03	8	4
(A) VO_2	350°C	tetrag.		11.90	11.90	7.68		1087.6		4.05	32	3
(B) VO_2	300°C + 440 MPa	mon.	$C2/m$	12.093	3.702	6.433	107.0	275.4		4.00	8	6
(A) VO_2	162°C	tetrag.	$P4_2/ncm$	8.434	8.434	7.678		546.2		4.02	16	7
(A_L) VO_2	162°C	tetrag.	$P4/ncc$	8.440	8.440	7.666		546.2		4.02	16	13
(A_H) VO_2		tetrag.	$I4/m$	8.476	8.476	3.824		274.7		4.01	8	13

[a] Abbreviations: mon., monoclinic; ortho., orthorhombic; tetrag., tetragonal.

noted S, is built up by endless double strings of VO_5 SP associated by corner sharing (14–16) (see Table 1). This structure is very similar to that of R–Nb_2O_5 (17) in which the shortening of the c-parameter is due to the establishment of the sixth Nb–O = 1.92 Å bond to build NbO_6 octahedra whereas the same V–O interatomic distance is 2.791 Å. Therefore, to facilitate the subsequent discussion, we opt for an ideal description of V_2O_5 made up of S layers of VO_6 octahedra interconnected via corner sharing (Fig. 1a). However, what occurs when V_2O_5 is reduced, by hydrogen for example? Théobald (18) gave a precise answer to this question. In the temperature range 200–400°C, V_4O_9 is formed, then (B) VO_2, the ultimate oxide being V_2O_3. Between 400–500°C, V_6O_{13} or (R) VO_2 rutile is obtained. Starting from VO_2,H_2O + a mixture of oxides exhibiting roughly 3.9–4.1 oxidation state under hydrothermal conditions (B) VO_2 is formed at 180°C and (A) VO_2 at 220°C.

The direct synthesis of (A) VO_2, which can only be achieved via hydrothermal methods, has been confirmed by Oka *et al.* (10).

SHEARING MECHANISM IN V_2O_5

The presence of double $[V_2O_5]_n$ layers is amply supported by several vanadium oxide bronzes (VOBs) detailed elsewhere (16). If an oxygen plane is removed in the V_2O_5 network with a 2c period, via hydrogen reduction, the structure can collapse according to three types of crystallographic shears (CS) (Fig. 1b), thus yielding structures with VO_2 stoichiometry:

(1) $CS = 1/6[103]$ (001), CS indicated by arrow B1 (Fig. 1b). A double layer is formed with quadruple endless strings of VO_6 octahedra sharing edges along [010]; these layers are named D4. Interconnected by corners along [001] they form the monoclinic (B) VO_2 (Fig. 1c).

(2) $CS = 1/6[-103]$ (001), CS indicated by arrow B2. The same type of double layer is formed, but its mirror image named D4m, yielding again (B) VO_2 (Fig. 1d). Note that both D4 and D4m layers exist in the ρ $K_xV_2O_5$ vanadium oxide bronze where they make an alternate ordered stacking of sandwiching potassium atom planes ...D4–K–D4m–D4... (19, 20).

(3) $CS = \frac{1}{2}[101]$ (001) (arrow A); an original double layer called Dz is formed by cross-linked double strings of VO_6 octahedra sharing edges and corners. Dz layers held together by corner sharing, via the untouched oxygen plane, form (A) VO_2 (Fig. 1e). Dz layers associated to D4 ones exist, making a nonordered packing separated by sodium atoms planes in the VOB intergrowth structure of τ $Na_xV_2O_5$(21).

Note that V_6O_{13} is obtained from the same crystallographic shear $CS = 1/6[103]$ (001) as (B) VO_2 but with a 3c repetition period along [001] in the V_2O_5 network. The sequence of layers connected by corners is ...D4–S–D4–S... The V_6O_{13} crystal structure has been determined by Aebi (22) and refined by Wilhelmi *et al.* also (23). V_6O_{13} and (B) VO_2 exhibit almost the same a and b parameters allowing for an easy topotactic association and tending to induce some confusion about VO_2 over stoichiometry in oxygen.

MECHANISM OF THE (B) $VO_2 \Rightarrow$ (A) VO_2 PHASE TRANSITION

Both (B) VO_2 and (A) VO_2 structures have been idealized in Figs. 2a and 2b where the cells are denoted by dotted lines. Crystallographic data are summarized in Table 1.

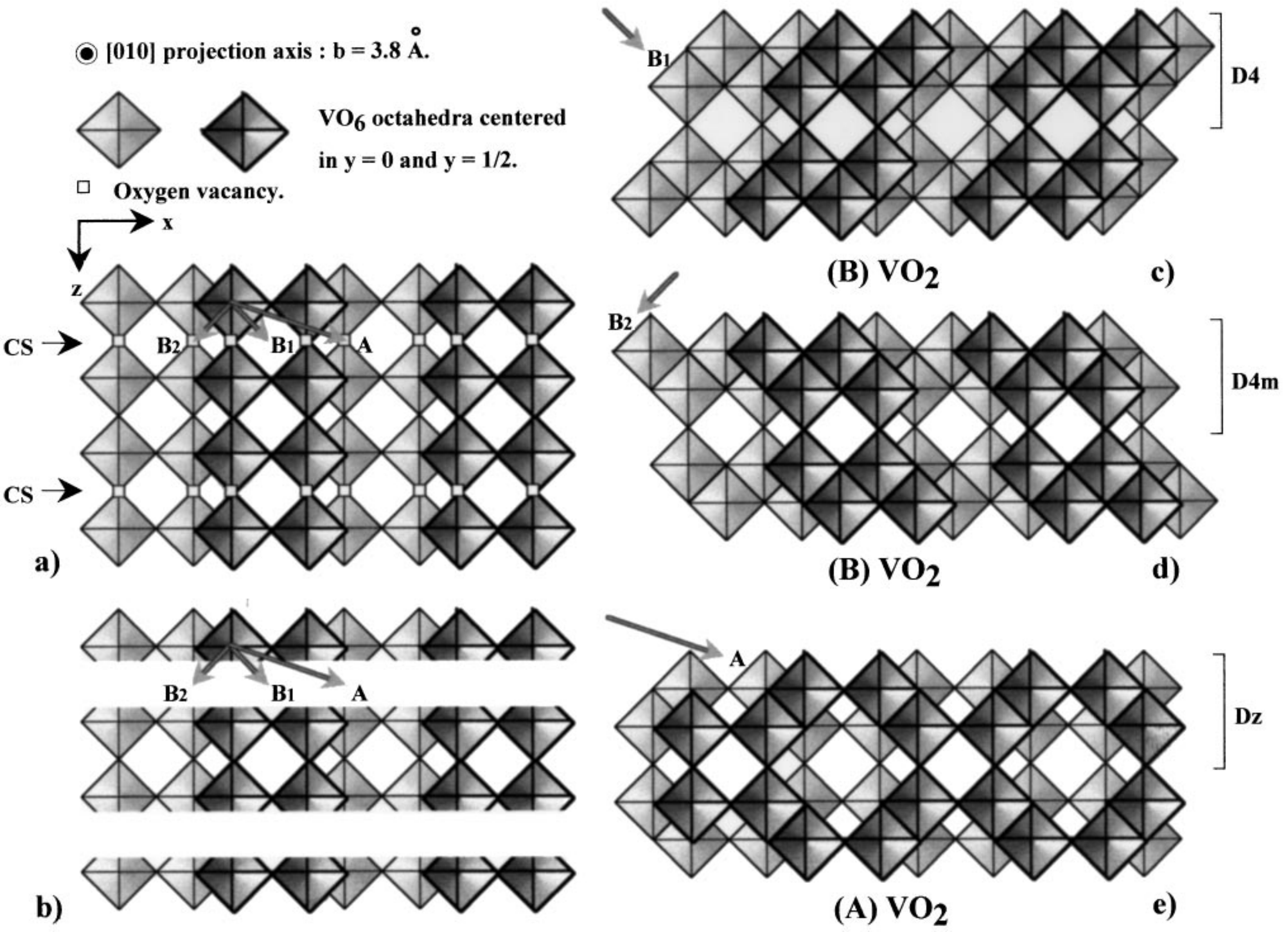

FIG. 1. (a) Crystallographic shears A, B1, and B$_2$ in the ideal V$_2$O$_5$ structure and indication of the potential sites for oxygen vacancies (*CS* repetition 2*c*). (b) Formal elimination of the oxygen planes. (c) Formation of D4 layers (B1) by $CS = 1/6[103](001)$. (d) Formation of D4m layers (B2) by $CS = 1/6[-103](001)$. (e) Formation of Dz layers (A) by $CS = \frac{1}{2}[101]\ (001)$.

Parameter *c* of (A) form is twice the value of *b* in (B) VO$_2$; nevertheless, the small tilting of VO$_6$ octahedra along the *c*-axis allows us to represent this structure as a projection along an axis ~3.8 Å as in B; such representation also corresponds to A$_H$ form. The most accurate data for A$_H$ and A$_L$ varieties (13) are listed in Table 1.

The essential point is the analysis of the V–O bonding in D4 and Dz. When separated, as in the M$_x$V$_2$O$_5$ VOBs, vanadium atoms shift toward the apices of the octahedra pointing toward the intercalated M atom's layer. The length of this V–O bond is typical of a V=O double bonding, i.e., ~1.60 Å. Perpendicular to the median plane of D4 and Dz, a long V–O bond ~2.2–2.3 Å appears opposite the V=O, which indicates a certain weakness in the association of the two single layers *S* by edge sharing.

In (B) and (A) structures, strong V–O bonds with the oxygen atoms along the *b* and *c* parameters are formed with those providing connection between successive D4 or Dz layers: V1–O1 = 1.721 Å and V2–O1 = 1.930 Å for the former and V–O2 = 1.993 and 1.784 Å for the latter. Opposite these bonds and perpendicular to the median plane (mp) of D4 and Dz layers are the weakest bonds V1–O2 = 2.318 Å and V2–O3 = 2.059 Å in the (B) form and V–O1 = 2.030 and 2.241 Å in the A form. For clarity, a schematic drawing is given in Fig. 3.

Of course the vanadium atoms are again displaced, although slightly less than in the VOB case, towards the oxygen shared by two consecutive double layers making up a strong V–O–V bonding ⟨V–O ~ 1.86 Å⟩. The strongest association in the structure is the double layer DS formed by two S layers associated by corners (see Fig. 2).

Thus, via a simple crystallographic slip $Cs = 1/3[-100]$ (001) applied in the median plane of the D4 layers of the (B) VO$_2$ structure, we can transform them into Dz layers and then build up the (A) VO$_2$ structure.

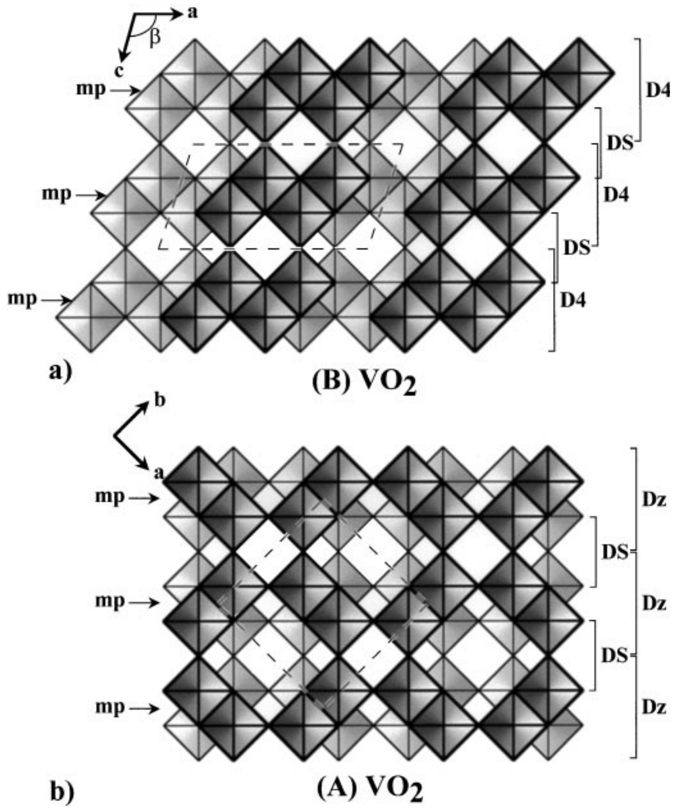

FIG. 2. Ideal representation projected along the ~ 3.8 Å axis of (a) (B) VO_2 monoclinic variety; (b) (B) VO_2 tetragonal variety. D4 and Dz double layers and their mp (median plane) are indicated. DS represents the double layer formed by two single S layers.

DISCUSSION

Formation of the (B) VO_2 phase by reduction of V_2O_5 and the related structural inference obtained by applying *CS* (B1 or B2) in the mother network are in good agreement. The *CS* A also explain why (A) VO_2 is not obtained via this type of synthesis, the implied atomic shifts being too large. The repetition of *CS* B along [001], $2c$ for VO_2 and $3c$ for V_6O_{13}, still making reasonable periodicity, appears more dubious for V_4O_9, implying a periodicity of $4c$. The structure of this oxide determined by Wilhelmi *et al.* is utterly different (24); we found exactly the same structure (25). V_3O_7 also shows an original structure (26, 27).

For the (B) $VO_2 \Rightarrow$(A) VO_2 transition, Oka *et al.* (10) proposed a mechanism based on the shift of oxygen vacancies along [100] in the fcc lattice with a rearrangement of vanadium atoms. This model occurs in the well-tightened part of the structure and implies fairly important jumps of the vanadium atoms. Our proposal based on the crystallographic slip Cs = 1/3[− 100](001) appears supported by Théobald's and Oka's experiments:

— (A) VO_2 only appears under hydrothermal conditions (4, 10), i.e., pressure;

— (A) VO_2 is induced mechanochemically, the transformation being accelerated by grinding, this being confirmed by X-ray diffraction powder patterns of samples treated at 300°C after compression under 440 Mpa for 5 min (9).

To summarize, under reducing conditions V_2O_5 can only yield V_6O_{13} and (B) VO_2 phases, but not (A) VO_2, this latter phase being obtained under metastable conditions when pressure effects are playing a significant role. Structural deduction of the (A) VO_2 network from V_2O_5 by a crystallographic shear *CS* operation, described for the first time, has resulted in a new way for the phase transition (B) towards (A). Finally, the (B) $VO_2 \Rightarrow$ (A) VO_2 transition is simply described by a crystallographic slip Cs occurring in the median plane of the double layers D4 of the monoclinic (B) VO_2, the mechanochemical activation breaking the weakest bonds of this structure and promoting a simple cooperative displacement to give the tetragonal (A) VO_2. The general scheme is

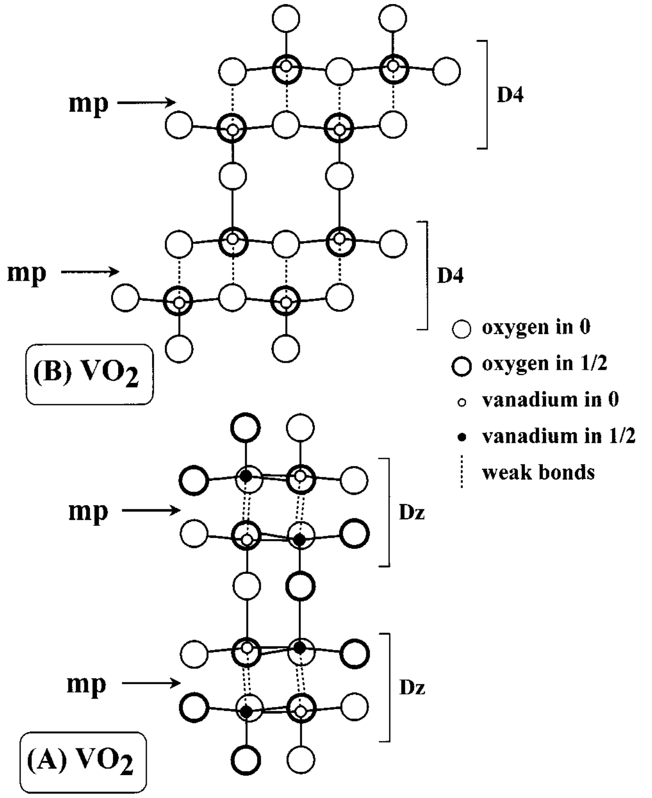

FIG. 3. Schematic drawing of the V–O bonding in both D4 and Dz layers of the (B) and (A) VO_2 phases, the dotted lines representing the weak bonding perpendicular to the mp (median plane) where the *Cs* = 1/3[− 100](001) occurs.

as follows:

$$\mathrm{V_2O_5} \overset{\text{Reduction}}{\underset{CS=1/6[103](001)}{\Rightarrow}} \mathrm{(B)\ VO_2} \overset{\text{Pressure}}{\underset{CS=1/6[-100](001)}{\Rightarrow}} \mathrm{(A_L)\ VO_2}$$

$$\overset{\text{Temperature}}{\Rightarrow} \mathrm{(A_H)\ VO_2}$$

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