From VO$_2$(B) to VO$_2$(R): Theoretical structures of VO$_2$ polymorphs and in situ electron microscopy

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The intermediate steps of the phase transition between the metastable monoclinic VO$_2$(B) phase and the stable tetragonal rutile VO$_2$(R) phase have been studied by in situ electron microscopy. A crystallographic interpretation based on the static concentration waves theory is proposed: as temperature increases, the long-range order in the complex monoclinic VO$_2$(B) phase is lost and gradually a first intermediate ill crystallized phase with a drastically reduced symmetry is formed as evidenced from the diffraction patterns. Next, a new tetragonal phase is generated that corresponds to a state where some of the vanadium atoms are now in a disordered state. When annealing inside the microscope, this phase grows out into a superstructure, with coexistence of two possible orientation variants. In all these phases the VO$_6$ octahedra remain virtually parallel, but for the final transition around 450 °C into the rutile stable phase, half of the octahedra have to reorient; the transition therefore has the aspects of a reconstructive one as is evident from the in situ experiment.

1. Introduction

Vanadium dioxide can adopt different structures. The most stable is the rutile one which, when heated at 68 °C, shows a reversible metal-insulator phase transition VO$_2$(M)→VO$_2$(R) associated with drastic changes in the optical properties such as a rapid decrease in optical transmittance in the near-IR region. Recently, thermochromic pigment of VO$_2$ has been used in a polymer composite coating. In order to obtain good coatings, the use of submicrometer powders of VO$_2$(R) is indispensable: the original method used in Ref. 1 to produce submicron thermochromic VO$_2$ powders involves an intermediate reduction step in which the VO$_2$(B) metastable allotropic phase is formed. The thermal decomposition of ammonium hexavanadate at 600 °C followed by pyrolysis at low temperature (≤380 °C), produces metastable VO$_2$(B): the transformation of this black, or bluish, nonthermochromic powder into rutile VO$_2$ is a crucial step for the final morphology that influences the optical properties.

Transformations between the different polymorphs of VO$_2$ were reported in the literature. Concerning the transformation with increasing temperature of VO$_2$(B) into VO$_2$(R), Theobald reported the sequence VO$_2$(B)→VO$_2$(A)→VO$_2$(R), which was realized by hydrothermal treatment. The VO$_2$(A) phase is metastable and has a tetragonal structure. However, Theobald specified that he did not observe the occurrence of VO$_2$(A) when starting from VO$_2$(B) under normal pressure. It seems that, starting from VO$_2$(B), this VO$_2$(A) phase can only be obtained under particular pressure conditions (hydrothermal treatment of the VO$_2$(B) phase). Oka, Yao, and Yamamoto confirmed the importance of pressure conditions in the growth of the VO$_2$(A) phase, starting from VO$_2$(B). The crystallographic relationships between VO$_2$(B) and VO$_2$(A) were studied by Oka, Yao, and Yamamoto; the unit cells of both phases are related by $c_A=2b_B$ and $a_A=2a_B+2c_B$, but it is quite obvious that the octahedra arrangement in both structures is very different. The transformation of VO$_2$(B) in VO$_2$(R) has also been studied recently by thermogravimetry and analysis and Fourier transform infrared spectroscopy methods under normal pressure and it has been shown that the transformation occurs at least in two stages. It certainly is not a simple transformation occurring at a fixed temperature. In this work, we have followed the transformation by electron diffraction and electron microscopy: the production of VO$_2$(R) by heating VO$_2$(B) up to 450 °C under low-pressure conditions, as it occurs in the electron microscope, to our knowledge has not been reported before.

II. Crystallography of Vanadium Dioxides

Generally speaking, the structures of the four VO$_2$ polymorphs, VO$_2$(R), VO$_2$(M), VO$_2$(B), and VO$_2$(A), are based on an oxygen bcc lattice with vanadium in the octahedral sites, the oxygen octahedra being more or less regular. They can be separated in two groups, depending on the mutual orientation of the fourfold axis of the oxygen octahedra. The oxygen octahedra can be aligned either along two perpendicular directions, as it is the case in rutile structure VO$_2$(R), and in monoclinic deformed VO$_2$(M); or oxygen octahedra can be mainly aligned along one direction as in VO$_2$(B) and VO$_2$(A). Note that these two groups correspond to two different values for the density (see Table I). It is clear that, although these VO$_2$ polymorphs correspond to the same stoichiometry, their structures are very different.

The most stable structure for vanadium dioxide is the so-called rutile structure VO$_2$(R), which is stable from 68 °C to 1540 °C: the tetragonal cell has parameters $a=b=4.55\ \text{Å}$, $c=2.88\ \text{Å}$, $Z=2$; the space group is $P4_2/mmm$ (136). Atomic positions are listed in Table II. This group gives rise to a very symmetric structure; vanadium atoms are...
TABLE I. Densities of VO₂ polymorphs.

<table>
<thead>
<tr>
<th>Density (g/cm³)</th>
<th>VO₂(R)</th>
<th>VO₂(M)</th>
<th>VO₂(B)</th>
<th>VO₂(A)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4.67</td>
<td>4.67</td>
<td>4.031</td>
<td>4.035</td>
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</tbody>
</table>

TABLE II. Atomic positions for VO₂(R).

<table>
<thead>
<tr>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2a</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

TABLE III. Atomic positions for VO₂(M).

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>4e</td>
<td>0.242</td>
<td>0.975</td>
</tr>
<tr>
<td>O1</td>
<td>4e</td>
<td>0.1</td>
<td>0.21</td>
</tr>
<tr>
<td>O2</td>
<td>4e</td>
<td>0.39</td>
<td>0.69</td>
</tr>
</tbody>
</table>

at the center of regular oxygen octahedra (two V-O bonds at 0.1933 nm, the four others at 0.1922 nm), with their fourfold axes aligned alternatively along [110] and [110] [see Fig. 1(a)]. The different octahedra share edges, building chains along the c axis of the structure [see Fig. 1(b)].

The formation at 68 °C of the monoclinic VO₂(M) is related to the appearance of a pairing between two V⁴⁺ along e_R. The induced distortion leads to a lowering of the symmetry. We obtain a monoclinic cell with cell parameters related to the rutile structure: a_M = 2e_R, b_M = a_R, c_M = b_R - e_R. The cell parameters of the room temperature phase VO₂(M) are a = 5.75 Å, b = 5.42 Å, c = 5.38 Å, β = 122.6°, Z = 4, the space group is P2₁/c (14). Atomic positions are listed in Table III.

In the VO₂(B) structure, there is also a pattern of octahedra aligned along two perpendicular directions [see Fig. 1(a)], but the octahedra are no longer regular. There is now one short distance V-O (0.176 nm) corresponding to a double link. The vanadium atoms have shifted from the center of the octahedra [see Fig. 1(a)] and form chains that are no longer parallel to the c axis (i.e., a_M) [Fig. 1(b)]. There are now two different distances between vanadium atoms 0.2615 and 0.3162 nm instead of 0.2851 nm for the rutile structure, leading to a doubling of the cell along the c axis of the rutile phase.

The two other polymorphs of VO₂ have little in common with the rutile phase. They have larger cells, with octahedra mainly aligned along one crystallographic direction. A monoclinic structure was proposed by Theobald, Cabala, and Bernhard for VO₂(B) obtained by gentle reduction (hydrothermal treatment) of V₂O₅. The parameters of the monoclinic cell are: a_B = 12.03 Å, b_B = 3.693 Å, c_B = 6.42 Å, and β = 106.6°, Z = 8 and the space group is C2/m (12). Atomic positions are listed in Table IV. The VO₂(B) structure can be considered as formed by two identical layers of atoms along b. Figure 3 shows the arrangement of octahedra in the (010) plane of VO₂(B): the second layer is shifted with respect to the first one by ½, ½, 0. In this structure, the oxygen octahedra are deformed, the vanadium atoms being no longer in their center; this leads to two types of octahedra. The ex-fourfold axes of the oxygen octahedra are more or less aligned along a single crystallographic direction, namely, [010]. Striking similarities exist between the VO₂(B) and the V₄O₁₃ structure. These similarities were already noticed in Ref. 10. Like V₄O₁₃, VO₂(B) forms platelets, their size depending on the preparation method. These platelets are preferentially oriented. They grow in (a,b) planes; this can be understood from Fig. 3 because in this plane one forms a network of corner sharing octahedra. VO₂(B) and V₆O₁₃ only differ in the way the octahedra are linked in the (a,b) plane; they exhibit a similar [001] diffraction pattern.

The other metastable phase of vanadium dioxide called VO₂(A) was first reported by Theobald, as an intermediate phase in the transformation VO₂(B) → VO₂(R); it has been fully characterized by Oka et al. VO₂(A) is tetragonal with cell parameters a = b = 8.44 Å, c = 7.68 Å, Z = 16, space group P42/nmc (138). Atomic positions are listed in Table V. Figure 4 shows a projection along the [001] direction. Like in VO₂(B), the fourfold axes of the oxygen octahedra are aligned along a single direction, in this case the c axis of the tetragonal structure. Note that this c parameter is roughly twice the b axis of VO₂(B); the oxygen octahedra are less deformed than in VO₂(B) and there is only one type of octahedron.
III. THEORETICAL DEDUCTION OF POSSIBLE STRUCTURES

A. General considerations

In order to study the transition from VO$_2$ ($B$) to VO$_2$ ($R$), we will unravel the structure of these two polymorphs. In both structures, the oxygens are distributed on a body-centered-cubic lattice and we will start from this oxygen lattice. Unless otherwise stated, all notations will refer to the bcc lattice. Vanadium atoms can be added to this lattice in octahedral sites. There are six possible octahedral sites for one bcc oxygen cell, two oxygen atoms. In a VO$_2$ compound, (one vanadium for two oxygens), $\frac{2}{3}$ of the octahedral sites will be empty and only $\frac{1}{3}$ site will be occupied. In a completely disordered phase vanadium atoms and their vacancies would be randomly distributed between the octahedral sites of the bcc host lattice. The elementary cell for a completely disordered phase would be the bcc lattice with slightly larger parameters and the resulting diffraction pattern would correspond to the reciprocal lattice of the bcc host lattice. The room-temperature diffraction patterns of VO$_2$ ($B$) or VO$_2$ ($R$) indeed exhibit strong reflections corresponding to the bcc positions. However, it is obvious that there are many supplementary spots, indicating that vanadium atoms and vacancies are ordered. This means that a high-temperature order-disorder phase transition is a possible scheme.

To deduce the ordered arrangements of the vacancies in the periodic structure, we will use the static concentration wave (SCW) method which, initially, was applied to describe ordering in substitutional-interstitial solid solutions and was then extended to the case of layer structures for some metal oxides by Khachaturyan and Pokrovskii.\textsuperscript{11}

The main idea is that the ordered structures will have new periodicities, as compared to the disordered one, and that they can be described by a superposition of static concentration waves with wave vectors $k_j$, corresponding to these new periodicities. The most stable structure will correspond to the minimum of the configuration energy. In an Ising model, we can define the interaction energy between two atoms, $W(R)$, and write it as a Fourier series on the SCW. This gives us the Fourier transform, $V(k_j)$, and its eigenvalues, $\lambda_n(k_j)$. It has been shown in Ref. 11, that the total configuration energy can then be written as a sum of these eigenvalues weighted by square modulus of the corresponding amplitudes. Then, to obtain the minimum energy, the amplitude $k_j$ that corresponds to the minimum $\lambda_n(k_j)$ must be maximal: this SCW will be called the dominant wave and its wave vector will be called $k_0$. This condition is the maximal amplitude principle, and we will use it further in our considerations.

As was shown by Khachaturyan and Pokrovskii,\textsuperscript{11} the maximum amplitude principle is automatically fulfilled if the wave vectors of the ordered structure are equal to $\frac{1}{2}$, $\frac{1}{3}$, and $\frac{1}{4}$ of a fundamental reciprocal lattice vector $H$ of the disordered crystal. However, in many layer structures, the wave vectors have arbitrary values, $H/n$ with $n>4$, and then the

| TABLE IV. Atomic positions for VO$_2$ ($B$). |
|---|---|---|
| V1 | 4i | 0.803 | 0.725 |
| V2 | 4i | 0.902 | 0.300 |
| O1 | 4i | 0.863 | 0.991 |
| O2 | 4i | 0.738 | 0.373 |
| O3 | 4i | 0.934 | 0.595 |
| O4 | 4i | 0.642 | 0.729 |

| TABLE V. Atomic positions for VO$_2$ ($A$). |
|---|---|---|
| V  | 16j | 0.1894 | 0.0176 | 0.0118 |
| O1 | 16j | 0.1674 | 0.0012 | 0.3743 |
| O2 | 8i  | 0.1634 | 0.3416 |
| O3 | 8i  | 0.1352 | 0.8930 |
dominant wave \( \mathbf{k}_0 \) should inevitably be supplemented with nondominant waves with wave vectors \( \mathbf{k}_s = x \mathbf{k}_0 \), where \( x \) is an integer and has a maximum value \( s_1 \), such that \( \mathbf{k}_s \) is not a vector of the reciprocal disordered lattice as long as \( s \leq s_1 \). The stability of these structures decreases with increasing \( s \) because, if we increase the number of nondominant waves, the configuration energy increases.

B. Ordering leading to \( \text{VO}_2(R) \)

We start from the bcc oxygen lattice. Following Pokrovskii and Kachaturyan, we divide the possible octahedral sites in three sublattices obtained by three different translations from a given oxygen position: \( [1/2, 0, 0] \) (\( \text{O}_a \) sublattice), \([0, 1/2, 0]\) (\( \text{O}_b \) sublattice), and \([0, 0, 1/2]\) (\( \text{O}_c \) sublattice); each sublattice has two possible sites for the vanadium atoms. The SCW theory allows us to estimate the change in energy induced by the possible ordering of vacancies; if the ordering decreases the energy, the ordered structure can be stable. It is clear that this theory cannot incorporate small structural deformations, induced by the appearance of interstitials and vacancies.

Pokrovskii and Kachaturyan have shown that the first ordering that can diminish the energy of the vanadium atoms is obtained for a dominant wave \( \mathbf{k}_0 = 0 \) (and no nondominant waves): (a) either if only one octahedral sublattice is filled (e.g., \( \text{O}_a \)); (b) or if only two sublattices are filled (e.g., \( \text{O}_b \) and \( \text{O}_c \)), the last one \( (\text{O}_a) \) being vacant. For both cases, the wave vector is \( \mathbf{k}_0 = 0 \) so that no new reflections appear: the diffraction patterns will be unmodified.

The last possibility, where we keep two types of octahedral sublattices, has two ordered vacancies on the \( \text{O}_a \) octahedral sublattice, which leaves us with three vacancies and one vanadium atom that are still disordered but have to be on the \( \text{O}_a \) and \( \text{O}_b \) sublattices. From this basic structure, two successive orderings (with \( \mathbf{k}_0 = 1/2, -1/2, 0 \) and \( \mathbf{k}_0 = 1/2, 1/2, 0 \)) lead Pokrovskii and Kachaturyan to the rutile structure. Note that all ordering schemes were obtained with only dominant waves so that the resulting structure will be stable. Taking into account the presence of vacancies and vanadium atoms on the three possible sublattices, the rutile \( \text{VO}_2 \) should be written as \( (\text{V}_{1/4} \square 3/4)_s \times (\text{V}_{1/4} \square 3/4)_s (\square)_c \text{O} \) where \( \square \) stands for a vacancy.

C. Initial ordering for \( \text{VO}_2(B) \)

\( \text{VO}_2(B) \) differs in many points from the rutile \( \text{VO}_2 \).

(a) Though the oxygen octahedra are deformed, we can still define their fourfold axes. In the case of \( \text{VO}_2(B) \) these axes are all parallel while for \( \text{VO}_2(R) \) they are along two perpendicular directions as explained before.

(b) The structure is very irregular, with condensed parts and less condensed parts. It is rather like the homologous series structures \( V_n \text{O}_{2n-1} \), where the vanadium atoms have different valences, though, in \( \text{VO}_2(B) \), all vanadium atoms have a valency 4.

(c) As already mentioned, the \( \text{VO}_2(B) \) structure is looser: this is macroscopically measured by a lower density. Moreover, the bcc oxygen lattice in \( \text{VO}_2(B) \) has one vacancy for eight occupied sites, while, in the rutile form, the bcc oxygen lattice is fully occupied.

These data about \( \text{VO}_2(B) \) suggested us to start from the idea to have only one octahedral sublattice filled (a possibility proposed by Pokrovskii and Kachaturyan). We then have four ordered vacancies on two of the octahedral sublattices \( \text{O}_a \) and \( \text{O}_c \), which will remain empty in all the successive possible orderings. There is only one vacancy and one vanadium atom left that can occupy the two sites of the \( \text{O}_b \) octahedral sublattice. As a consequence, the \( c \) axis will be elongated (Fig. 5) and the cell is now tetragonal rather than cubic. If the \( c \) axis reaches the value of \( a \sqrt{2} \) the centered tetragonal cell can be rewritten as a face-centered-cubic cell. Indeed, the oxide \( \text{VO} \) exists and has a \( \text{NaCl} \) structure; its parameter is 0.406 nm, and which would give a parameter \( a \approx 0.29 \) nm for our starting bcc cell. In \( \text{VO} \), however, the vanadium appears as \( V^{2+} [2 R(O^{2-}) + 2 R(V^{4+})] \approx 0.44 \) nm while in \( \text{VO}_2(B) \) it appears as \( V^{4+} \), which implies a smaller ionic radius. Indeed, the fourfold axes of the octahedra in \( \text{VO}_2(B) \) have a length equal to 0.369 nm to be compared with \( 2 R(O^{2-}) + 2 R(V^{4+}) \) which is \( \approx 0.39 \) nm.

To better understand our starting structure, we first draw the “ideal” \( \text{VO}_2(B) \), i.e., we put all the atoms (vanadium or oxygen) on the exact sites they would occupy in the undistorted bcc lattice. SCW theory will never produce these small displacements anyway. The resulting structure is depicted in Fig. 6 and the two main corresponding diffraction patterns appear in Fig. 7. The oxygen atoms form a centered lattice that is tetragonal rather than cubic, with cell dimensions 0.29 and 0.37 nm. The monoclinic \( \text{VO}_2(B) \) and the initial body-centered lattices are related in the following way:

\[
\mathbf{a}_0 = 3 \mathbf{a} + 3 \mathbf{b}, \quad \mathbf{a}^* = 1/9(2 \mathbf{a}^* + \mathbf{b}^*),
\]


\[ \mathbf{b}_B = \mathbf{c}, \quad \mathbf{b}_B^* = \mathbf{c}^*. \]

\[ \mathbf{c}_B = \mathbf{a} - 2 \mathbf{b}, \quad \mathbf{c}_B^* = \frac{1}{3}(\mathbf{a}^* - \mathbf{b}^*). \]

The correspondence between some planes and directions in both systems is given in Table VI. If we take into account the intensities of the different structure factors, we see that all the reflections that do not correspond to a bcc reciprocal lattice can be generated from only two additional waves, the \( \frac{1}{3}(1, -1, 0) \) [(001)\( \beta \)] and the \( \frac{2}{3}(2,1,9) \) [(110)\( \beta \)]. We therefore have two possibilities for calculating the VO\(_2\)\( (B) \) structure: either start from the structural data given above to choose the waves that are introduced as compared to the oxygen bcc lattice or calculate and minimize an evaluation of the vanadium system energy.

The result of this first ordering of vacancies that will be the start for the further orderings can be written as \( (\Box)_x(\Box)_y \) (disordered \( \text{V}_{1/2}\Box_{1/2} \text{O} \)).

**D. Further orderings for VO\(_2\)\( (B) \): from structural data**

We have two independent superstructure waves that appear in the diffraction pattern of VO\(_2\)\( (B) \) as compared to the bcc lattice. Hence, we need two different successive orderings to reach VO\(_2\)\( (B) \).

We start from a disordered situation (see before) where all sites are occupied by \( \text{V}_{1/2}\Box_{1/2} \) and we want to reach an ordered structure where one half of the sites are fully occupied by vanadium atoms (and \( \frac{1}{3} \) are vacant). The SCW \( \frac{1}{3}(1, -1, 0) \) can only order \( \frac{1}{3} \) (or \( \frac{2}{3} \)) of the vacancies leaving \( \frac{2}{3} \) (or \( \frac{1}{3} \)) possible sites for vacancies. The SCW \( \frac{2}{3}(2,1,9) \) can order a fraction \( n/9 \) of vacancies, where \( n \) is an integer, leaving \( (9-n)/9 \) sites for vacancies. The resulting number of ordered vacancies will be \( \frac{1}{3} \) (or \( \frac{2}{3} \)) multiplied by \( (9-n)/9 \) and has to be \( \frac{1}{3} \) (or very near it). The only solution is \( n = 3 \) giving the final formula \( (\Box)_x(\Box)_y(\text{V}_{49}\Box_{50})\text{O} \).

Starting ordering the bcc lattice with the SCW \( \frac{2}{3}(2,1,9) \) as a dominant wave implies that we must also have nondominant waves. The ordering induced by this SCW is given by the so-called clock diagram (Fig. 8) where we order three vacancies planes. It leads to the following sequence of \( (2,1,9) \) planes \( \Box\Box\Box\times\times\times\times\Box\Box\Box\times\times\times\times\Box\Box\Box\times\times\times\times\times\times\times\times\times\times \times \) where \( \times \) stands for planes that can be occupied by vanadiums and vacancies while \( \Box \) stands for a completely empty plane. The resulting structure is shown in Fig. 9(a).

The second ordering is applied on the remaining possible sites for vanadiums (planes marked \( \times \)) and is given by the dominant wave \( \frac{1}{3}(1, -1, 0) \). The corresponding occupation probability is then

\[ n(x,y,z) = \frac{1}{3} - \frac{1}{3} \cos[2\pi(x-y)/3]. \]

This means vacancies will be located on every third \( (1, -1, 0) \) plane, when \( x-y = 3p \) where \( p \) is an integer \( n(x,y,z) \) is then equal to 0. The corresponding structure is shown in Fig. 9(b) and would correspond to a formula \( \text{V}_{49}\Box_{50} \text{O} \) or \( \text{V}_3\text{O}_9 \). We remark that an equivalent ordering would have been obtained with the dominant wave \( \frac{1}{3}(2,1,3) \) : this is obvious in real space [Fig. 9(b)] but can also be understood because the two waves are equivalent.

**TABLE VI. Correspondence between planes and directions in the monoclinic and bcc lattices of VO\(_2\)\( (B) \).**

<table>
<thead>
<tr>
<th>VO(_2)( (B) ) Monoclinic cell</th>
<th>bcc cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>( (0,2,0) )</td>
<td>( (0,0,2) )</td>
</tr>
<tr>
<td>( (1,1,0) )</td>
<td>( 1/9(2,1,9) )</td>
</tr>
<tr>
<td>( (0,0,1) )</td>
<td>( 1/3(1, -1, 0) )</td>
</tr>
<tr>
<td>([1 0 6])</td>
<td>([1 - 1 0])</td>
</tr>
<tr>
<td>([0 0 1])</td>
<td>([1 - 2 0])</td>
</tr>
</tbody>
</table>
The groups are linked by identical but translated groups in successive orderings along two families of planes parallel to the reciprocal vector \( \mathbf{c} \).

This remark is interesting as it shows that the \( \text{VO}_2(B) \) structure is obtained by two successive orderings along two families of planes parallel to the \( c_B \) axis.

This heterogeneous distribution, however, will obviously induce unequal chemical potential values for different oxygen atoms. Such a system cannot be stable. This nonequilibrium situation is usually changed by introducing small displacements of atoms and/or by the creation of vacancies in the host lattice. In our case, we can see that one oxygen atom [marked by an arrow on Fig. 9(b)] is only loosely linked to the vanadium atoms as it does not belong to any octahedron. An oxygen vacancy will be very easily formed on that site when the vanadium atoms as it does not belong to any octahedron.

The structure can be described as consisting of groups of filled \((2,1,9)\) planes separated by groups of vacant planes. The groups are linked by identical but translated groups in the upper and lower planes perpendicular to \(c\).

E. Further orderings for \( \text{VO}_2(B) \):

by minimization of the energy

We start again from the \(((\Box),(\Box))\), (disordered \(\text{V}_{(1/2,1/2,1/2)}\)) structure. Following the SCW theory, we calculate the Fourier transform \(W\) of the energy of this tetragonal system. Vanadium atoms have eight nearest neighbors at a distance of \(\frac{a^2+b^2}{2}\), four atoms at \(a\), two at a distance of \(c\) and four at \(a\sqrt{2}\). We have taken into account the fact that, now, the \(c\) axis has a parameter larger than the \(a\) (or \(b\)) parameter but that it is probably less than \(a\sqrt{2}\) (see earlier). We obtain for \(W\):

\[
W = 8X_1\cos\pi k_x \cos\pi k_y \cos\pi k_z + 2X_2(\cos 2\pi k_x + \cos 2\pi k_y)
+ 2X_3\cos 2\pi k_y + 4X_4\cos 2\pi k_x \cos 2\pi k_z,
\]

where \(X_1, X_2, X_3,\) and \(X_4\) are constants for the interactions with the first, second, third, and fourth neighbors: \(X_1 > X_2 > X_3 > X_4 > 0\). \(k_x, k_y,\) and \(k_z\) are the components of a reciprocal vector \(\mathbf{k}\), which characterizes the concentration wave generated by the ordering. The minimum energies are easy to obtain when only one dominant wave is present,\(^1\) this corresponds to a vector \(\mathbf{k}\) equal to a bcc reciprocal vector \(\mathbf{H}\), divided by 2, 3, or 4. In the first Brillouin zone, all the possibilities are in the stars listed herein: \(\mathbf{H}/2:\{000\}, \{100\}, \{1 1 0\}; \mathbf{H}/3:\{1 0 0\} \{1 2 0\}, \{1 1 2\}; \mathbf{H}/4:\{1 1 1\}, \{1 2 0\}, \{1 1 0\}, \{1 0 0\}\).

The minimum energy is obtained for the star \(\{1 1 2\}\); among the members of this star, we can choose whichever wave seems more suitable for our description as all the waves in the star will give rise to the same structure. The value of \(W\) is the same for all members of the star and is \(W(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) = -X_1 - 2X_2 - X_3 + X_4\); this corresponds to a large decrease in energy. Remembering the results obtained in the previous paragraph, we choose either \(\mathbf{k}_1 = \frac{1}{2}(2,1,1)\) or \(\mathbf{k}_1 = \frac{1}{2}(1, -1, 2)\) as the dominant wave. The corresponding occupation probabilities of the sites in the only remaining octahedral sublattice \(\text{O}_2\) are

\[
n(x,y,z) = \frac{1}{2} - \frac{1}{3} \cos[2\pi(x+y+2z)/3] = \frac{1}{2} - \frac{1}{3} \cos[2\pi + y + z]/3)\text{.}
\]

This means vacancies will be located on every third \((1, -1, 2)\) plane when \(x+y+2z = 3p\) where \(p\) is an integer.
...FROM VO$_2$ (B) TO VO$_2$ (R): THEORETICAL ...

Let us call $\mathbf{H'}$ a reciprocal lattice vector of the second ordering. We have to find a vector $\mathbf{k'} = \mathbf{H'}/n$ with $n = 2, 3, \text{or} 4$, which minimizes $W'$. A minimum is obtained for the vector $\mathbf{k'} = 1/3(1,1,2)$. This wave corresponds to a rather small decrease in energy: $W' = -2X_2 - X_3 + 2X_4$ as can be expected for a ternary ordering. This last ordering with the vector $\mathbf{k'_2}$ would restore the tetragonal symmetry and lead to a structure $(V_{49}\square_{50})O$ and to VO$_2$ (A).$^{14}$

However, as already pointed out by Khachaturyan,$^{13}$ our energy model is rather crude and we have to accept that other vectors, near the ones considered above, might give smaller or identical minima. However, these vectors will no longer be half, third, or fourth of the host lattice reciprocal vectors. Following the procedure outlined in Ref. 13 we find that two possibilities can, indeed, provide a lower minimum: $\mathbf{k'_2} = (2,1,9)/9$ for which the value of $W'$ is $-4.76X_1 + 1.88X_2 + 2X_3 - X_4$; $\mathbf{k'_2} = (4,2,6)/9$ for which the value of $W'$ is $-0.88X_1 - 1.53X_2 - X_3 + 0.35X_4$.

We now have dominant and secondary waves. If we take into account the fact that $X_1$ and $X_2$ are very similar (they correspond to interactions between atoms situated at nearly equal distances) and that the same holds for $X_3$ and $X_4$ we see that the energy variations are about the same. However, $\mathbf{k'_2}$ exists in the reciprocal space of VO$_2$ (B) while $\mathbf{k'_2}$ does not. This $\mathbf{k'_2}$ vector generates a layer structure perpendicular to $\mathbf{k'_2}$. The proportion of vacant planes must be $n/9$, $n$ being an integer. Since we want a stoichiometry as near as possible to $\frac{1}{9}$ we choose $n = 3$. To deduce the sequence of full and vacant planes, we again use the clock diagram: the three vacant planes are sequential. We then obtain the structure shown in Fig. 11. For each plane perpendicular to $c$, one obtains the atomic arrangement of the VO$_2$ (B) structure. As in the previous paragraph one oxygen atom is not stable: hence, a vacancy will be created. The piling up of these planes along $c$, however, is no longer the same as in VO$_2$ (B) but gives rise to a very heterogeneous distribution and only small translations perpendicular to the $c$ axis are needed to obtain the VO$_2$ (B) structure.

In summary, we can say that VO$_2$ (B) derives from a bcc lattice where vanadium atoms are introduced along with vacancies, on the octahedral interstices. Successive ordering of these vacancies can create stable structures that could form a homologous series. The successive orderings shown here lead to a formula $V_nO_{9n}$ where one of the oxygen atoms is in an unstable position and will be replaced by a vacancy: all vanadium ions then have a valency $+4$.

**IV. IN SITU ELECTRON MICROSCOPY STUDY OF VO$_2$ (B)→VO$_2$ (R)**

VO$_2$ (B) powder is crushed and mixed with alcohol before being dispersed on a Cu grid covered with holey carbon. Experiments are performed in a 120 kV or in a 200 kV electron microscope. The temperature of the heating holder is measured by a thermocouple, but the exact temperature of the crushed material is hard to determine accurately.

The initial powder mainly consists of thin and long plate-like monocrystals with a monoclinic structure. The diffraction patterns are in good agreement with the VO$_2$ (B) structure determined by Théobald. VO$_2$ (B) platelets are mostly...
oriented along [001]₀ or along a direction perpendicular to the (a, b) planes, which is [1 0 6]₀. In Fig. 12(a), we show the calculated diffraction pattern for the [001]₀ direction, while, in Fig. 12(b) we have calculated the diffraction pattern for a direction near the [1 0 6]₀ direction where we have taken into account some relaxation of the Bragg conditions due a size effect associated with defects (medium deviation to the Ewald sphere, s = 0.1 Å⁻¹). The patterns differ in the intensity distribution of some spots but, geometrically, they are identical. Figure 12(c) shows the experimental diffraction pattern. This will be our starting orientation for the heating experiment, the electron beam being roughly perpendicular to the (a, b) plane. On the low magnification images of Fig. 13(a), a number of planar defects are present; their origin is clear from high-resolution electron microscopy images such as Fig. 13(b). They are identified as twin interfaces with the twin plane being the (100) plane. The zero-order Laue zone of the [001]₀ section is insensitive to twinning but the [1 0 6]₀ is not, which explains why we can see the effect of the twinning, as a slight difference in background contrast. This confirms, if needed, that the electron beam is not exactly along the [001] direction.

During heating, we observe a strong change in the microstructure of the platelike monocrystals associated with important modifications of the diffraction patterns.

The first change in reciprocal space is the vanishing, around 200 °C, of most of the long-range order reflections such as 200 and 400 [Fig. 14(a)]; only the 601 (or 600), 020- and 110-type reflections maintain their intensity. At a later stage the 110 reflections also strongly decrease in intensity. This implies that the long-range order of the octahedra (Fig. 8) is mostly destroyed. In order to explain the vanishing of the superstructure reflections one has to assume a breaking of the interconnections between different octahedra, which are either corner sharing or edge sharing in the VO₂(B) structure.

As the VO₂(B) reflections disappear, other reflections appear, mainly associated with the reflections 601₀ and 020₀; they are indicated by X and Y in Fig. 14(b); at first sight, the X spots look more like satellites and do not form a superstructure while the Y spots are regularly aligned between bcc-type spots. Note that fourfold symmetry is not restored and that the splitting is asymmetrical. This X structure, however, is restricted to nanosize domains and can be shown to correspond to symmetric orientations of a monoclinic intermediate structure with an angle slightly different from 90°.

The other reflections in Fig. 14(b), marked Y, cannot be explained on the basis of this monoclinic distortion; they must have a different origin. Upon careful further heating (not passing the rutile transition) one can see the X-type reflections vanish [Fig. 14(c)] while the Y reflections develop to form a true superstructure [see Fig. 14(d)]. This pseudo-tetragonal diffraction pattern clearly consists of two orientation variants, rotated 90° with respect to each other. This is, e.g., evident in the initial stages in Fig. 14(b) where one variant is much stronger than the other. The diffraction patterns shown in Figs. 14(b) and 14(d) can be compared to the calculated diffraction pattern Fig. 11 obtained in Sec. III.

In real space, one can follow the morphology of the platelets during the heating experiment. The platelet shape is
maintained as long as one does not reach the temperature where the rutile phase is formed. Fig. 15(a) shows the same platelet as in Fig. 13(a), but at a temperature near the transition temperature; the corresponding diffraction pattern is shown Fig. 14(c). Although the shape of the platelet remains, it consists now of two types of domains, roughly oriented perpendicular to each other, and at 45° of the twins interfaces existing in the initial VO₂(B) platelet.

Upon continued heating, the platelets abruptly break up into nanocrystallites and recrystallize into the rutile structure [Fig. 15(b)]. Such breaking up is clearly necessary in view of the completely different arrangement of the VO₆ octahedra in both structures. No orientation relationship exists between the phase VO₂(B) and the rutile phase, nor between neighboring rutile type grains. Remarkably, no oxygen is lost during this complete transformation cycle, although the morphology and the shape of the crystal does change drastically during the transition.

V. DISCUSSION AND CONCLUSION

The phase transition from VO₂(B) to VO₂(R) is remarkable and very unusual. While VO₂(B) as well as VO₂(A) and all related structures- is based on an ordered arrangement of single axis aligned octahedra, the rutile form of VO₂ is built up from octahedra aligned along two mutually perpen-

FIG. 13. (a) Low magnification image of one VO₂(B) platelet. (b) lattice fringes image showing the (1,1,0), the (−1,1,0), and the (2,0,0) planes.

FIG. 14. Evolution of the diffraction patterns during the heating experiment. (a) first stage; disappearance of spots characteristic of the VO₂(B) structure, (b) second stage; new spots appear, (c) third stage; disappearance of spots marked X, (d) final stage before the formation of VO₂(R) crystals; diffraction pattern with a tetragonal symmetry.
Scanning calorimetry measurements show that the transition intrinsic character of this transition. However, the differential of 120 kV or vacuum of the electron microscope under an electron irradiation of a platelet, taken just before the transformation into crystals of VO$_2$(R) occurs. (b) Final crystals of VO$_2$(R).

However before the octahedra more or less break apart and order themselves along two perpendicular axes, a lot of rearrangement and reshuffling has taken place within the structure. This is the first time these changes have been carefully recorded and their structure analysed. The fact that this transition has been studied inside the structure. This is the first time these changes have been carefully recorded and their structure analysed.

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10 F. Theobald, R. Cabala, and J. Bernard, J. Solid State Chem. 17,