DEFECT STRUCTURES IN V₂O₅ AND ITS LOWER OXIDES

L. FIERMANS, P. CLAUWS AND W. DEKEYSER
Laboratorium voor Kristallografie en Studie van de Vaste Stof, Rijksuniversiteit Gent, Krijgslaan 271, B-9000 Gent, Belgium

ABSTRACT

It is shown that in the transitions V₂O₅→V₄O₁₃ and V₄O₁₃→V₆O₁₉, two lattice defects play an important role, i.e., the vanadyl-oxygen vacancy and shear structures. The former has been unambiguously characterized by IR absorption spectroscopy and EPR. The latter has also been characterized in the same way, but the spectra are more complex and not readily identified. It is consequently proposed that V₄O₁₃ is an ordered superstructure of vanadyl-oxygen vacancies in a slightly distorted V₂O₅ matrix, whereas V₆O₁₉ can be described as a shear structure of V₄O₁₃ with shear vector 1/6 [103].

INTRODUCTION

In recent years it has become clear that many interesting properties of solids are due to the presence and the interaction of small numbers of lattice defects. Departures from stoichiometry are a characteristic of a large variety of compounds. Nonstoichiometry is related to lattice defects, and thus correlated with the properties of the compound. Such studies have, for obvious reasons, been performed on simple and very pure compounds. Transition metal oxides (TMO) have been extensively studied in this respect. A large variety of compositions and structures of TMOs exist. Crystallographic shear permits, in a number of cases, a simple interpretation of the transition of one structure into another. In this brief review we will be concerned with V₂O₅ and its lower oxides. Large and pure single crystals of V₂O₅ have been grown in our laboratory and have been extensively studied. Suboxides and structural defects have been studied with a variety of techniques such as LEED, AES, XPS, IR absorption spectroscopy and EPR. The role played by various defects in the transitions of V₂O₅ into its lower oxides has been particularly investigated. The main defect, the vanadyl-oxygen vacancy, was characterized in detail with IR and EPR. In this brief review a summary is given of these investigations.

V₂O₅ AND ITS LOWER OXIDES

V₂O₅ has an orthorhombic structure with lattice parameters a 11.510, b 3.563, c 4.369 Å (Bachmann et al. 1961). The unit cell contains two formula units; the space group is Pmmn. Figure 1 gives a schematic representation of the structure in which the building block is a deformed octahedron; the shortest distance corresponds to a vanadyl bond (V=O: 1.585 Å). The longest V–O distance (2.785 Å) is a weak van der Waals bond. V₂O₅ consequently has a layer structure in which (001) is a plane of easy cleavage.

Two superstructures of V₂O₅ resulting from oxygen loss have been reported, i.e., the 7-fold and the 24-fold superstructures (Tilley & Hyde 1970). Both are described as being ordered-vacancy structures in a V₂O₅ matrix.

A compound V₄O₁₃ has been described by various authors (Tudo & Tridot 1965, Thomas et al. 1967, Waltersson et al. 1974). It has a monoclinic structure with lattice parameters a 21.921, b 3.679, c 18.341 Å, β 95.61°. The space group is C 2/c.

Two different compounds with composition V₆O₁₉ but different structures are described in the literature. In what follows, a model for this oxide based on results obtained in our labo-
The proposed space group in $Pnma$ or $Pn2a$. According to Théobald et al. (1969), however, $V_2O_5$ has a tetragonal structure with lattice parameters $a = 8.235$, $b = 10.138$ Å. Possible space groups proposed by these authors are $P4_{2}nm$, $P4_{nc}$, $P4/mnc$ and $P4_{2}/mmn$. According to results obtained by Grymonprez et al. (1977), $V_2O_5$ is an ordered-vacancy structure in a slightly distorted $V_2O_5$ matrix, and consequently has an orthorhombic structure. The $V_2O_5$ structure has been obtained from $V_2O_5$ by electron bombardment in an electron microscope (Tilley & Hyde 1970). Annealing in UHV of an air-cleaved $V_2O_5$ single crystal also results in a $V_2O_5$ phase, which grows topotactically on the $V_2O_5$ substrate. A set of X-ray diffraction lines (Table 1) can be interpreted as the 2nd, 4th, ..., 10th order reflections of net planes with $d_{221} = 16.4$ Å. Indeed, as will be shown in what follows, oscillation photographs of this layer could only be indexed assuming a third lattice parameter of approximately 16.47 Å.

From the structure model of $V_2O_5$ we will propose, however, it is not possible to determine the space group unambiguously.

Four different structures of composition $V_{2}O_{13}$ ($V_{4}O_{13}$) are described in the literature (Aebi 1948, Théobald et al. 1968, Sata & Ito 1969). We will restrict ourselves to a description of the structure proposed by Aebi (1948). According to this author $V_2O_5$ has a monoclinic structure with lattice parameters $a = 11.922$, $b = 3.680$, $c = 10.138$ Å, $\beta = 100.87^\circ$. The projection of this structure on (010) is represented in Figure 2. In the $c$ direction, contrary to what is the case in $V_2O_5$, there is no alternation of vanadyl and van der Waals bonds. Consequently, $V_2O_5$ does not cleave as easily as does $V_2O_5$. The space group is $C2/m$.

Horiuchi et al. (1975) have been able to illustrate the $V_2O_5$ structure by electron microscopy. Under the influence of the electron beam, a transformation into a phase VO$_2$ occurs, according to a transition mechanism closely resembling the one we present here for the transition $V_2O_5 \rightarrow V_2O_5$.

**TABLE 1.** X-RAY DIFFRACTION LINES OF $V_2O_5$ GROWN TOPOTACTICALLY ON $V_2O_5$ (001)

<table>
<thead>
<tr>
<th>$d_{hkl}$</th>
<th>relative intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.19</td>
<td>2.5</td>
</tr>
<tr>
<td>4.12</td>
<td>2.6</td>
</tr>
<tr>
<td>2.74</td>
<td>weak</td>
</tr>
<tr>
<td>2.06</td>
<td>3</td>
</tr>
<tr>
<td>1.65</td>
<td>0.5</td>
</tr>
</tbody>
</table>

**Fig. 2.** Schematic representation of the projection on the (010) plane of the $V_2O_{13}$ structure. The octahedra are represented as being perfect.
transition, which occurs at higher temperatures, involves the shearing of whole layers with respect to one another; $V_2O_5$ is a shear structure of $V_2O_6$ (Wadsley 1955, Colpaert et al. 1973).

**The transition $V_2O_5 \rightarrow V_4O_9$**

The first step in the reduction of $V_2O_5$ is the formation of the 7-fold superstructure, obtained by thermal treatment of thin $V_2O_5$ single crystals in vacuum at 100°C (Tilley & Hyde 1970). At 150°C the phase $V_O$ is obtained (called $V_O$ by Tilley & Hyde, but the identity $V_O = V_2O_5$ was shown by Grymonprez et al. 1977). Thermal treatment at higher temperatures (up to 550°C) results in reduction to $V_4O_9$.

$V_2O_5$ crystals have been investigated in our laboratory using X-ray oscillation photographs. Characteristics of $V_4O_9$ are in agreement with the reciprocal lattice derived by Tilley & Hyde from a high-energy electron diffraction pattern of $V_O$. As mentioned above there exists a certain degree of confusion concerning the symmetry of $V_4O_9$. Table 2 summarizes the lattice parameters.

As our oscillation photographs could only be indexed assuming a third lattice parameter of approximately 16.47 Å, we conclude that $V_4O_9$ has an orthorhombic structure as originally proposed by Tilley & Hyde, with lattice parameters as indicated in the last column of Table 2. The topotactic growth of $V_2O_5$ on $V_4O_9$ mentioned above has led to our assumption that there is a structural relationship between $V_2O_5$ and $V_4O_9$. It was furthermore noticed that the density of $V_4O_9$ (3.25) and the density 3.228 of a hypothetical structure $V_4O_9$ derived from $V_2O_5$ by removal of 10% of the oxygen are in very close agreement. These observations suggested the possibility that the structure of $V_4O_9$ was closely related to a superstructure of $V_2O_5$. Such a structure was described by Grymonprez et al. (1977).

Consider the projection of the $V_2O_5$ structure on the $a-b$ plane and assume that one tenth of the O atoms is removed in the manner indicated in Figure 3. Figure 4 shows the projection of this hypothetical superstructure on (100). It can be shown that the characteristics of this superstructure and those of the $V_4O_9$ structure are practically identical. The minor differences are easily explained by distortions in the proposed superstructure.

A driving force for these distortions seems to be the repulsive interaction between oxygen vacancies. Other models are possible in which the oxygen vacancies are located on other sites, but in the same arrangement. The model in which the vacancies are located on vanadyl

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**Table 2. Lattice Parameters of $V_4O_9$**

<table>
<thead>
<tr>
<th></th>
<th>$V_4O_9^1$</th>
<th>$VO_2^2$</th>
<th>$V_4O_9^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>8.235 Å</td>
<td>8.1 Å</td>
<td>8.235 Å</td>
</tr>
<tr>
<td>$b$</td>
<td>8.235</td>
<td>10.4</td>
<td>10.32</td>
</tr>
<tr>
<td>$c$</td>
<td>10.32</td>
<td>16.1</td>
<td>16.47</td>
</tr>
</tbody>
</table>

1 Théobald et al. (1969); 2 Tilley & Hyde (1970); 3 Grymonprez et al. (1977).

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**Fig. 3.** Projection of the $V_2O_5$ structure on the (001) plane showing the removal of one tenth of the O ions, giving rise to a model for $V_4O_9$ with ordered vacancies (after Grymonprez et al. 1977).
Fig. 4. Projection of the hypothetical superstructure model for \( \text{V}_2\text{O}_5 \) on the (100) plane (after Grynonprez et al. 1977).

The transition \( \text{V}_2\text{O}_5 \rightarrow \text{V}_4\text{O}_{12} \)

This transition occurs by thermal treatment at higher temperatures (> 400°C). A standard treatment leading to topotactic growth of a \( \text{V}_4\text{O}_{12} \) layer on a \( \text{V}_2\text{O}_5 \) substrate consists of cleaving a \( \text{V}_2\text{O}_5 \) single crystal in air, giving it a pretreatment at approximately 300°C in approximately \( 10^6 \) Pa (1 atm.) oxygen, followed by a UHV heat treatment at 550°C. The fact that \( \text{V}_4\text{O}_{12} \) grows topotactically on the \( \text{V}_2\text{O}_5 \) substrate can be explained by the close relationship between the two structures. This can easily be understood in terms of the shear structures. The oxygen vacancy seems to be most likely, however, because it has been shown that vanadyl oxygen is the most reactive in catalytic oxidation reactions on \( \text{V}_2\text{O}_5 \) catalysts. From the foregoing we conclude that the reduction of \( \text{V}_2\text{O}_5 \) at low temperatures, probably via non-stoichiometric \( \text{V}_2\text{O}_5 \) in which randomly distributed oxygen vacancies occur, proceeds by an ordering of the vanadyl–oxygen vacancies, resulting in the formation of a 7-fold superstructure and eventually, of a slightly distorted superstructure of composition \( \text{V}_4\text{O}_{12} \). It seems thus established that in the transition \( \text{V}_5\text{O}_{10} \rightarrow \text{V}_6\text{O}_{10} \) the vanadyl–oxygen vacancy plays an important part.
Point defects in \( \text{V}_2\text{O}_5 \) can be studied by their IR and EPR spectra. We have investigated the spectra of the vanadyl--oxygen vacancy and of substitutional and interstitial donors (Clauw \& Vennik 1974, 1975; Gillis \& Boesman 1966, Boesman \& Gillis 1966, Vanhaelst \& Clauws 1978). The near infrared absorption spectrum (0.2--2.2 eV) of undoped \( \text{V}_2\text{O}_5 \) single crystals is a superposition of different absorption bands, labeled \( \text{Fl}, \text{F2}, \text{F3} \) (Fig. 8), where \( \text{Fl} \) is composed of bands at 1.52 and 1.25 eV (\( E//a \)), and 1.05 eV (\( E//b \)) (Clauw \& Vennik 1974). The magnitude of \( \text{Fl} \) is almost constant in all samples grown in 10\(^5\) Pa (\( \text{O}_2 \)). Crystals grown in air and samples homogeneously reduced in 10\(^5\) Pa (\( \text{N}_2 \)) (650 °C) or UHV (550 °C), on the other
Fig. 8. Absorption spectrum of undoped \( \text{V}_2\text{O}_5 \) single crystal. 1: as-grown; 2: annealed in \( \text{O}_2 \) (650°C) for 48 hours; 3: annealed in \( \text{N}_2 \) (650°C) for 48 hours.

hand, exhibit an increased intensity of F1. Reoxidation reduces the intensity to its original level.

During a recent EPR study of \( \text{V}_2\text{O}_5 \), a spectrum different from the well-known spectrum of the \( \text{V}^{4+} \) centre with a vanadyl bond present was detected, located at higher magnetic fields. This new spectrum was labeled E1 (Vanhaelst & Clauws 1978). The dependence of its intensity on reduction and reoxidation was the same as the one observed for F1; F1 and E1 were consequently attributed to the same centre, related to the nonstoichiometry of \( \text{V}_2\text{O}_5 \). Both spectra were assigned to the electrons of the vanadyl-oxygen vacancy, considered to be a double donor. This assignment is supported by the EPR results. Indeed, E1 can be described by a spin Hamiltonian with effective spin \( S = 1 \), in agreement with the picture of a two-electron centre. The \( g \) values are quite different from the ones of a \( \text{V}^{4+} \) centre forming a vanadyl bond (Clauws & Vennik 1975, Boesman & Gillis 1966). Therefore, the vacancy is assumed to be a vanadyl-oxygen vacancy. The high number of hyperfine splitting lines in E1 (about 20) indicates that the electrons interact with several vanadium nuclei. These electrons are located in the orbitals of several vanadium neighbors. The concentration of the vacancies is almost constant in as-grown crystals, and can be influenced by homogeneous reduction and reoxidation at elevated temperatures. The other IR and EPR spectra present in our undoped crystals are believed to be due to residual interstitial donors, such as Li, Na, K, Cu . . .

In this case the donor electron is localized on the four equivalent nearest V neighbors around the interstitial site. The corresponding IR spectrum of doped crystals exhibits an absorption band at 0.5 eV (F3) and the EPR spectrum contains 29 hyperfine splitting lines.

In our undoped crystals, a spectrum with 15 lines (localization on 2V ions) commonly dominates the EPR spectrum. It is transformed into the 29-line spectrum by the thermal treatments described above. The disappearance of the 15-line spectrum is accompanied by a decrease of the IR spectrum F2 (Clauws & Vennik 1974). We believe that F2 and the 15-line spectrum are typical of a perturbed interstitial site. The annealing would then remove the perturbation, resulting in the F3 band and the 29-line spectrum. From our experiments it follows that two models for this perturbation of the interstitial site have to be considered. The first involves the formation of an interstitial-vacancy complex, the second the presence of shear planes.

Further experiments are necessary to choose between the two. If the second possibility is at the origin of the perturbation, the occurrence of F2 and the 15-line spectrum could be an indication of the presence of shear planes, of could consequently be of importance in the study of the previously described transitions of \( \text{V}_2\text{O}_5 \) into its lower oxides.

DISCUSSION AND CONCLUSIONS

A common feature of the two reduced states of \( \text{V}_2\text{O}_5 \) considered here is that they can be understood in terms of the formation of vanadyl-oxygen vacancies, and the removal of different amounts of the latter from the \( \text{V}_2\text{O}_5 \) lattice. Of course, although the vanadyl-oxygen vacancy is thus considered as being the basic defect formed during reduction, the actual reduction product is determined by several factors we have not dealt with in detail in this review.
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These factors are, e.g., the initial state of the V$_2$O$_5$ surface and temperature.

At rather low temperatures (\(< 350^\circ\text{C}\)), the superstructures and V$_2$O$_5$ dominate; at higher temperatures V$_4$O$_9$, V$_3$O$_{13}$ and VO$_2$ are preferentially formed. This is believed to be related to the necessary rearrangement of oxygen polyhedra in the formation of the latter phases, as opposed to the relatively minor displacements involved in the formation of superstructures. In this respect, shear structures are considered to be the second basic defect in the formation of lower vanadium oxides. It is further believed that similar shear structures are likely to appear in the V$_4$O$_9$ lattice. As shown by Grymonprez et al. (1977), a simple model can be constructed to derive V$_3$O$_{13}$ from further reduction from V$_4$O$_9$. This clearly supports the idea that the creation of shear planes and of vanadyl-oxygen vacancies are important mechanisms for the reduction of V$_2$O$_5$.

REFERENCES


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