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DEFECT STRUCTURES IN V_2O_5 AND ITS LOWER OXIDES*

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ABSTRACT

It is shown that in the transitions $V_2O_5 \rightarrow V_4O_9$ and $V_2O_5 \rightarrow V_6O_{13}$, 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 V_4O_9 is an ordered superstructure of vanadyl-oxygen vacancies in a slightly distorted V_2O_5 matrix, whereas V_6O_{13} can be described as a shear structure of V_2O_5 with shear vector 1/6 $[10\bar{3}]$.

SOMMAIRE

Deux défauts de réseau jouent un rôle important dans les transitions de V_2O_5 à V_4O_9 et de V_2O_5 à V_6O_{13}; à savoir, les lacunes d'oxygène du vanadyle et une structure de glissement (shear). Le premier défaut a été identifié sans ambiguïté par spectroscopie d'absorption infrarouge et par résonance paramagnétique électronique; le second l'a été de la même façon, quoique les spectres fussent plus complexes et malaisés à interpréter. En conséquence, nous concluons que V_4O_9 possède une surstructure ordonnée de lacunes d'oxygène du vanadyle dans une matrice de V_2O_5 légèrement déformée, tandis que V_6O_{13} représente une structure de glissement obtenue à partir de V_2O_5 avec vecteur de cisaillement égal à 1/6 $[10\bar{3}]$.

(Traduit par la Rédaction)

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 *TMO*s 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 V_2O_5 and its lower oxides. Large and pure single crystals of V_2O_5 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 V_2O_5 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.

V_2O_5 AND ITS LOWER OXIDES

V_2O_5 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. V_2O_5 consequently has a layer structure in which (001) is a plane of easy cleavage.

Two superstructures of V_2O_5 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 V_2O_5 matrix.

A compound V_3O_7 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 V_4O_9 but different structures are described in the literature. In what follows, a model for this oxide based on results obtained in our labo-

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*A tribute to Professor J. D. H. Donnay.

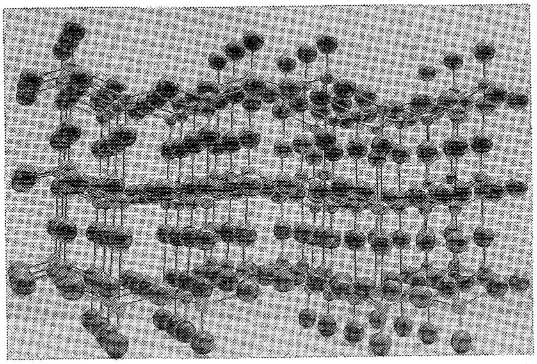

FIG. 1. Model of the V_2O_5 structure. The (001) planes are horizontal, the *a* direction being in the plane of the figure. The large spheres represent oxygen ions, the smaller ones vanadium ions.

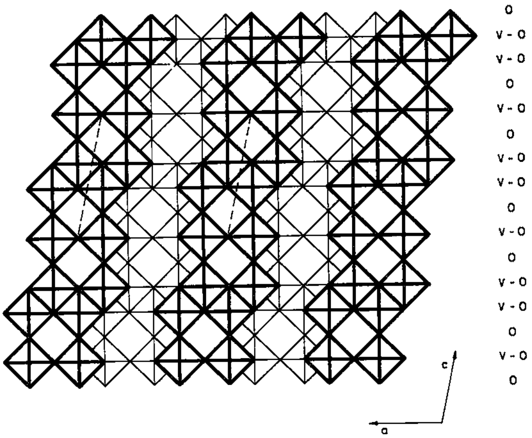

FIG. 2. Schematic representation of the projection on the (010) plane of the V_6O_{13} structure. The octahedra are represented as being perfect.

ratory will be presented (Grymonprez *et al.* 1977). According to Wilhelmi & Waltersson (1970) V_4O_9 has an orthorhombic structure with lattice parameters *a* 17.925, *b* 3.631, *c* 9.306 Å The proposed space group in *Pnma* or *Pn*2_1*a*. According to Théobald *et al.* (1969), however, V_4O_9 has a tetragonal structure with lattice parameters *a* 8.235, *c* 10.32 Å. Possible space groups proposed by these authors are *P*4_2*nm*, *P* 4*nc*, *P*4/*mnc* and *P*4_2/*mnm*. According to results obtained by Grymonprez *et al.* (1977), V_4O_9 is an ordered-vacancy structure in a slightly distorted V_2O_5 matrix, and consequently has an orthorhombic structure. The V_4O_9 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_4O_9 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_{hkl} = 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_4O_9 we will propose, however, it is not possible to determine the space group unambiguously.

TABLE 1. X-RAY DIFFRACTION LINES OF V_4O_9 GROWN TOPOTACTICALLY ON V_2O_5 (001)

d_{hkl}	relative intensity
8.19	2.5
4.12	2.6
2.74	weak
2.06	3
1.65	0.5

Four different structures of composition $VO_{2.17}$ (V_6O_{13}) are described in the literature (Aebi 1948, Théobald *et al.* 1968, Sata & Ito 1968). We will restrict ourselves to a description of the structure proposed by Aebi (1948). According to this author V_6O_{13} has a monoclinic structure with lattice parameters *a* 11.922, *b* 3.680, *c* 10.138 Å, *β* 100.87°. 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_6O_{13} does not cleave as easily as does V_2O_5. The space group is *C*2/*m*.

Horiuchi *et al.* (1975) have been able to illustrate the V_6O_{13} 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 $V_2O_5 \rightarrow V_6O_{13}$.

DEFECT STRUCTURE AND TRANSITIONS OF V_2O_5 INTO LOWER OXIDES

It will be shown that in the transitions $V_2O_5 \rightarrow V_4O_9$ and $V_2O_5 \rightarrow V_6O_{13}$ two defect structures play an important role, *i.e.*, the vanadyl–oxygen vacancy and ordered arrangements thereof, and stacking faults characterized by partial dislocations. Both defects have been characterized by IR absorption bands and EPR spectra. The $V_2O_5 \rightarrow V_4O_9$ transition proceeds *via* the formation of an ordered arrangement of vanadyl–oxygen vacancies. The $V_2O_5 \rightarrow V_6O_{13}$

transition, which occurs at higher temperatures, involves the shearing of whole layers with respect to one another; V_6O_{13} is a shear structure of V_2O_5 (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_4O_9 is obtained (called VO_x by Tilley & Hyde, but the identity $VO_x = V_4O_9$ was shown by Grymonprez *et al.* 1977). Thermal treatment at higher temperatures (up to 550°C) results in reduction to V_6O_{13}.

V_4O_9 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 VO_x. 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_4O_9 on V_2O_5 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).

TABLE 2. LATTICE PARAMETERS OF V_4O_9

	V_4O_9[1]	VO_x[2]	V_4O_9[3]
a	8.235 Å	8.1 Å	8.235 Å
b	8.235	10.4	10.32
c	10.32	16.1	16.47

[1] Théobald *et al.* (1969); [2] Tilley & Hyde (1970); [3] 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

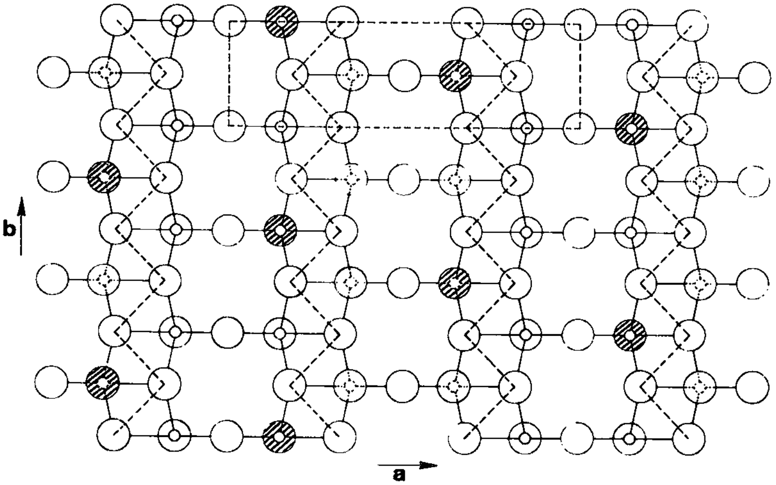

FIG. 3. Projection of the V_2O_5 structure on the (001) plane showing the removal of one tenth of the O ions, giving rise to a model for V_4O_9 with ordered vacancies (after Grymonprez *et al.* 1977).

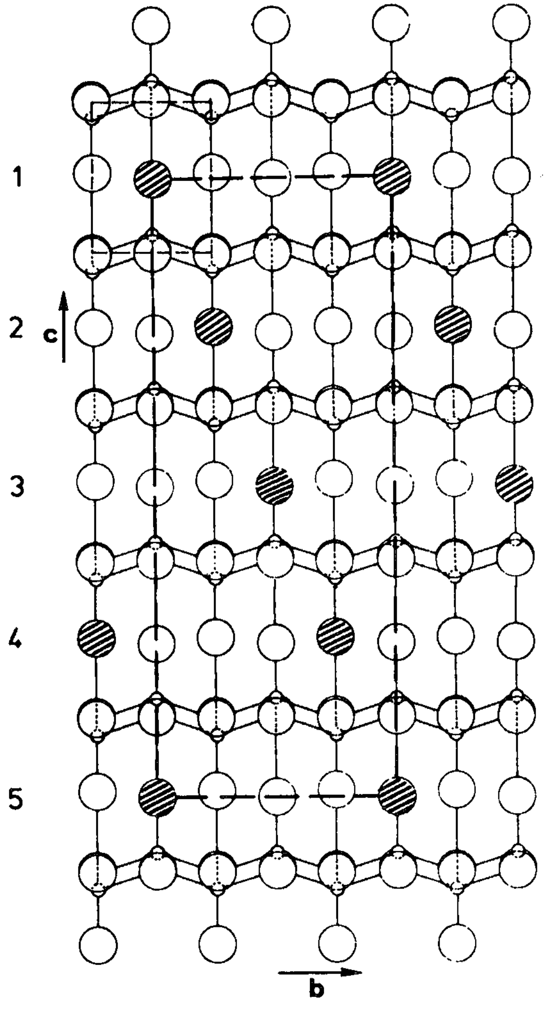

FIG. 4. Projection of the hypothetical superstructure model for V_4O_9 on the (100) plane (after Grymonprez *et al.* 1977).

oxygens seems to be most likely, however, because it has been shown that vanadyl oxygen is the most reactive in catalytic oxidation reactions on V_2O_5 catalysts. From the foregoing we conclude that the reduction of V_2O_5 at low temperatures, probably *via* non-stoichiometric V_2O_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 V_4O_9. It seems thus established that in the transition $V_2O_5 \rightarrow V_4O_9$ the vanadyl–oxygen vacancy plays an important part.

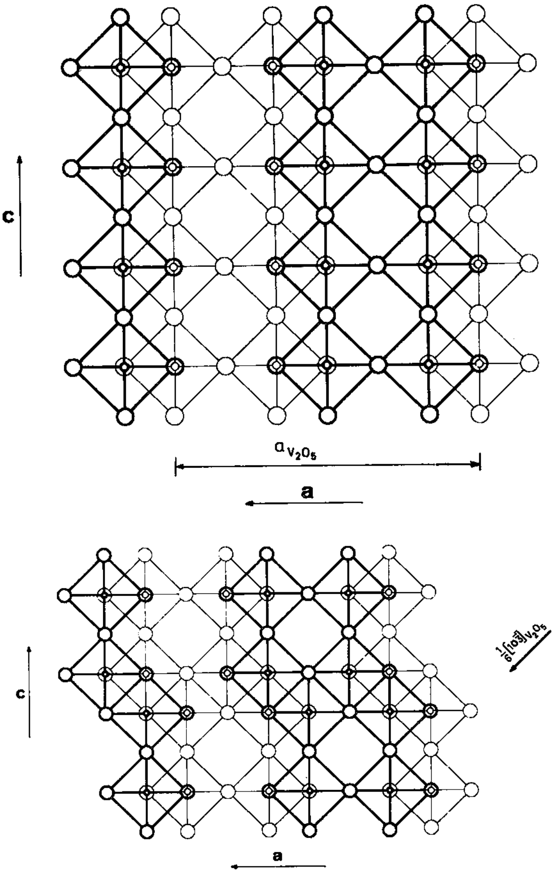

FIG. 5. Schematic representation of the introduction of shear planes in the V_2O_5 structure: (a) idealized V_2O_5 structure; (b) introduction of a (001) shear plane with shear vector $b = 1/6$ $[10\bar{3}]$; this corresponds to the V_6O_{13} structure.

The transition $V_2O_5 \rightarrow V_6O_{13}$

This transition occurs by thermal treatment at higher temperatures (> 400°C). A standard treatment leading to topotactic growth of a V_6O_{13} layer on a V_2O_5 substrate consists of cleaving a V_2O_5 single crystal in air, giving it a pretreatment at approximately 300°C in approximately 10^5 Pa(1 atm.) oxygen, followed by a UHV heat treatment at 550°C. The fact that V_6O_{13} grows topotactically on the V_2O_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

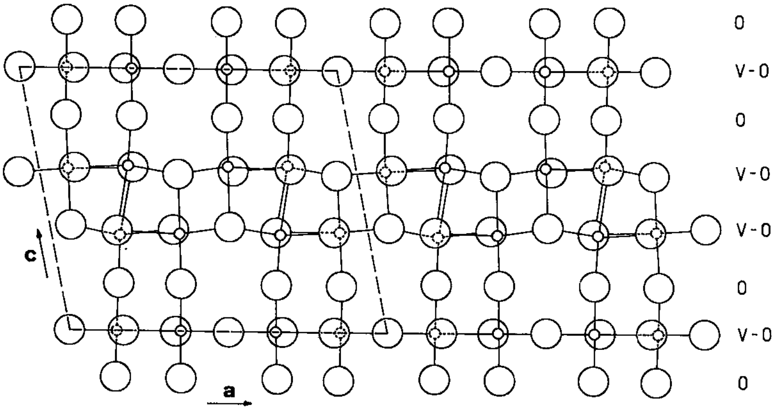

FIG. 6. Projection of the real V_6O_{13} structure on the (010) plane (after Aebi 1948).

V_6O_{13} structure can be obtained from the V_2O_5 structure by introducing in the latter (001) shear planes with shear vector $b = 1/6\ [10\bar{3}]$ at each third (001) plane, and removing the vanadyl oxygen from this plane. This is demonstrated in Figures 5a and 5b (where for the sake of simplicity, as in previous figures, the distorted octahedral units of V_2O_5 are substituted by regular octahedra). The real structure (Aebi 1948) is shown in Figure 6.

It is interesting to note that in V_2O_5, $1/6\ [10\bar{3}] = 1/6\ [100] + 1/2\ [00\bar{1}]$. An intermediate step in the formation of the shear structure is shown in Figure 7. This kind of deformation of the V_2O_5 lattice with fault vector $b \leqq 1/6\,[100]$ is thought to occur when local stress is present, *i.e.*, near the boundaries of inclusions of a different composition. As a consequence of the steric hindrance between the vanadyl–oxygen atoms in the distorted region, it is plausible to assume that they are less strongly bound than in the perfect bulk and can be removed more easily. It is clear that if these oxygen atoms are removed, a supplementary collapse in the c direction can follow. In this way shear planes with $b = 1/6\ [10\bar{3}]$ result and the corresponding V_6O_{13} structure is finally obtained.

It has been shown that the thermally induced $V_2O_5 \rightarrow V_6O_{13}$ transition can be understood in terms of a surface reaction involving the formation of vanadyl–oxygen vacancies (Colpaert *et al.* 1973). The extension of the transformed zone into the bulk clearly involves oxygen diffusion. The strained region formed by the border between V_2O_5 and V_6O_{13} could play a critical part in this process; the presence of partial dislocations (*i.e.*, stacking faults) is important in this respect.

IR ABSORPTION AND EPR SPECTRA OF DEFECTS IN V_2O_5

Point defects in V_2O_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 (Clauws & Vennik 1974, 1975; Gillis & Boesman 1966, Boesman & Gillis 1966, Vanhaelst & Clauws 1978). The near infrared absorption spectrum (0.2–2.2 *e*V) of undoped V_2O_5 single crystals is a superposition of different absorption bands, labeled F1, F2, F3 (Fig. 8), where F1 is composed of bands at 1.52 and 1.25 *e*V ($E/\!/a$), and 1.05 *e*V ($E/\!/b$) (Clauws & Vennik 1974). The magnitude of F1 is almost constant in all samples grown in 10^5Pa (O_2). Crystals grown in air and samples homogeneously reduced in 10^5 Pa (N_2) (650°C) or UHV (550°C), on the other

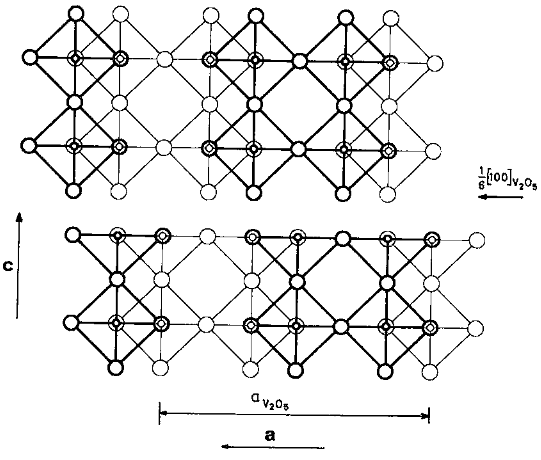

FIG. 7. Intermediate step in the transition $V_2O_5 \rightarrow V_6O_{13}$, with fault vector $b \leqq 1/6\ [100]$.

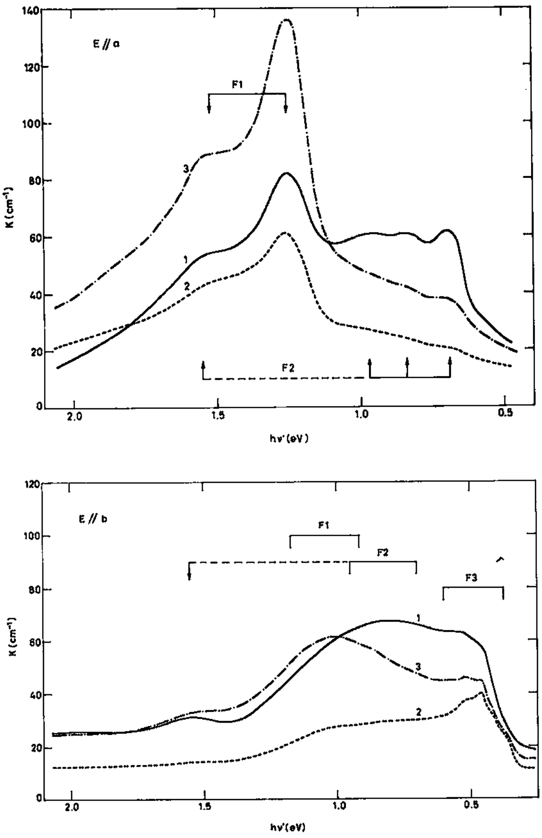

FIG. 8. Absorption spectrum of undoped V_2O_5 single crystal. 1: as-grown; 2: annealed in O_2 (650°C) for 48 hours; 3: annealed in N_2 (650°C) for 48 hours.

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

During a recent EPR study of V_2O_5, a spectrum different from the well-known spectrum of the 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 V_2O_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 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 *e*V (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 V_2O_5 into its lower oxides.

DISCUSSION AND CONCLUSIONS

A common feature of the two reduced states of V_2O_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 V_2O_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.

These factors are, *e.g.*, the initial state of the V_2O_5 surface and temperature.

At rather low temperatures (< 350°C), the superstructures and V_4O_9 dominate; at higher temperatures V_3O_7, V_6O_{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_4O_9 lattice. As shown by Grymonprez *et al.* (1977), a simple model can be constructed to derive V_6O_{13} by further reduction from V_4O_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_2O_5.

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