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Structural Properties of Vanadium Oxides

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It is shown that two vanadium oxides of unknown composition, *i.e.* VO_x [Tilley & Hyde, *J. Phys. Chem. Solids*, (1970), **31**, 1613–1619] and phase *Q* [Colpaert, PhD Thesis, Rijksuniv. Gent (1972)] are identical with V_4O_9 [Théobald, Cabala & Bernard, *C. R. Acad. Sci. Paris, Sér. C*, (1969), **269**, 1209–1212]. The unit cell of V_4O_9 is orthorhombic, with $a = 8{\cdot}235$, $b = 10{\cdot}32$, $c = 16{\cdot}47$ Å. A model for the structure of V_4O_9 is proposed. It is based on an ordered superlattice of O vacancies in V_2O_5, and is in agreement with X-ray oscillation photographs. The model accounts for the low density of this material, its low temperature of formation, the typical appearance of twins and the topotaxic growth of V_4O_9 on V_2O_5.

I. Introduction

Several vanadium oxides are known in the composition range V_2O_5–VO_2, *i.e.* V_2O_5 (Bachmann, Ahmed & Barnes, 1961), a 7-fold and a 24-fold superstructure of V_2O_5 (Tilley & Hyde, 1970), V_3O_7 (Tudo & Tridot, 1965), V_4O_9 (Wilhelmi & Waltersson, 1970; Théobald, Cabala & Bernard, 1969), V_6O_{13} (Aebi, 1948; Théobald, Cabala & Bernard, 1968; Sata & Ito, 1968), VO_2 (Andersson, 1954; Théobald & Bernard, 1969; Horiuchi, Saeki, Matsui & Nagata, 1975), VO_x (Tilley & Hyde, 1970), phase *Q* (Colpaert, 1972). Some of these compounds can adopt more than one structure. Only a few of them have been completely determined. For a few phases (VO_X, *Q*), the composition was hitherto also unknown. A detailed analysis of the reduction mechanism of V_2O_5 into lower oxides has led us to the study of the latter two phases.

II. Results and discussion

1. *Vanadium oxide phase Q* (*Colpaert*, 1972)

Thermal treatment in ultra-high vacuum (550 °C, 24 h) of an air-cleaved V_2O_5 single crystal leads to the formation of a phase of unknown composition, labelled *Q* by Colpaert who showed that it grew topotaxically on the V_2O_5 single crystal. When the treated V_2O_5 single crystals were mounted with the V_2O_5 (001) plane, *i.e.* the cleavage plane, parallel to the specimen holder of a diffractometer, four lines attributed to this phase were recorded. The corresponding values of d_{hkl} are 8·24, 4·11, 2·06 and 1·65 Å, *i.e.* the lines are even orders of a set of planes with interplanar distance 16·48 Å. The X-ray diffraction spectrum also contained the V_2O_5 lines, and a number of weak V_6O_{13} lines.

Using the same technique we obtained an identical set of lines for V_2O_5 single crystals, reduced with sulphur at low temperatures (200–320 °C). Topotaxically grown *Q*-phase material could be obtained in a crystallographically pure state by reducing V_2O_5 single crystals at 250 °C for 50 h in a sulphur atmosphere. After this material was ground, an X-ray powder diagram was obtained which corresponded to the spectrum attributed by Théobald, Cabala & Bernard (1969) to V_4O_9. Prolonging the treatment led to the formation of VO_2 (phase *B*, Théobald & Bernard, 1969). At temperatures above 250 °C, phase *B* appeared before all V_2O_5 was reduced to V_4O_9.

2. *X-ray oscillation photographs*

The reduced V_2O_5 single crystals had cracks along their crystallographic directions showing clearly that the topotaxic V_4O_9 surface layer has a specific orientation with respect to the V_2O_5 lattice. X-ray oscillation diagrams were made with *b* of the original V_2O_5 as oscillation axis and *c* bisecting the 15° oscillation angle.

The diffraction spots were located on two sets of sinusoidal curves instead of on one set of straight layer lines (Fig. 1). The combination of the two sets of curves forms an image which is symmetric with respect to the horizontal and vertical lines through the centre of the film. Hence, the reduced V_2O_5 crystals contain two lattices symmetrically located with respect to the (100) plane of the original V_2O_5 lattice. The separate lattices have a zone axis slightly inclined with respect to the oscillation axis and located in the plane perpendicular to the $c(V_2O_5)$ axis. Neither the plane perpendicular to this zone axis, nor the plane formed by this zone axis and the $c(V_2O_5)$ axis is a symmetry plane for the separate lattices.

The angle between the corresponding zone axes is $\alpha = 4°$ (the angle between each of these axes and the $b(V_2O_5)$ axis is 2°). The periodicity along these zone axes, 6·6 Å, was obtained from oscillation photographs

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recorded with one of these axes as oscillation axis (referred to as position I).

An image with the described characteristics can be obtained from a combination of reciprocal lattices (Fig. 2). The direction **I** corresponds to the zone axis of the reciprocal lattice indicated by open circles.

Oscillation photographs taken with direction **II** as oscillation axis (*i.e.* after turning the crystal in the plane perpendicular to the $c(V_2O_5)$ axis by 42° with respect to position I) gave an image in which part of the spots are located on straight horizontal lines. These spots are located symmetrically with respect to the vertical and the horizontal lines through the centre of the film. After turning the crystal in the plane perpendicular to the $c(V_2O_5)$ axis by 52° with respect to position I, the direction **III** is parallel to the oscillation axis. An oscillation photograph in this position shows the same characteristics as for position II. The periodicity along direction **II** lies between 10·2 and 10·3 Å, and along direction **III** between 8·2 and 8·3 Å. An accurate measurement of the periodicities was impossible because of an elongation of the diffraction spots.

3. VO_x (*Tilley & Hyde*, 1970)

The results obtained from our oscillation photographs are in agreement with the reciprocal lattice of the phase VO_x (Tilley & Hyde, 1970; Fig. 4). From this we conclude that VO_x is identical with V_4O_9 (and to phase *Q*).

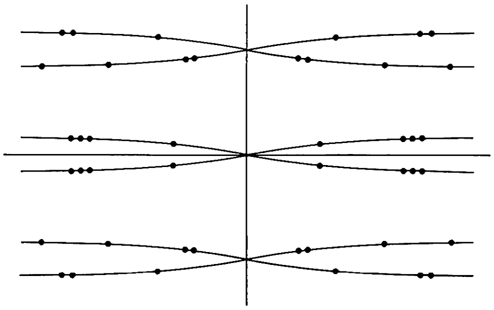

Fig. 1. Schematic representation of the X-ray oscillation photograph obtained from V_4O_9 topotaxic (001) surface layers on a V_2O_5(001) substrate.

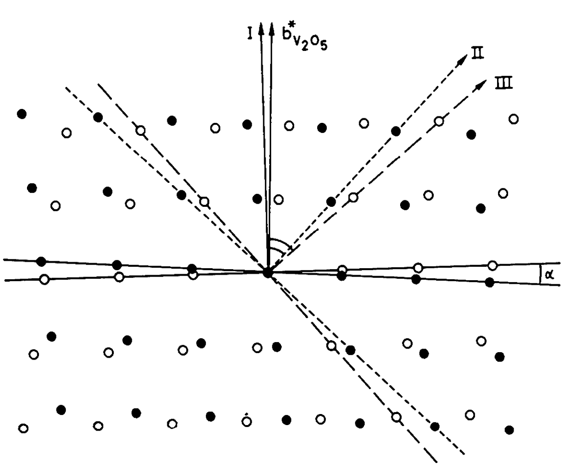

Fig. 2. Reciprocal mesh of a topotaxic V_4O_9(001) layer on top of a V_2O_5(001) substrate (Fiermans & Vennik, 1969).

4. V_4O_9

Théobald, Cabala & Bernard (1969) indexed the X-ray diffraction spectrum of V_4O_9 on a tetragonal structure, while Tilley & Hyde (1970) assumed an orthorhombic structure for VO_x. The respective lattice parameters are summarized in Table 1.

Table 1. V_4O_9 *lattice parameters* (Å)

V_4O_9 (Théobald *et al.*, 1969)	VO_x (Tilley & Hyde, 1970)	This work
$a=8·235$	$a=8·1$	$a=8·235$
$b=8·235$	$b=10·4$	$b=10·32$
$c=10·32$	$c=16·1$	$c=16·47$

Taking into account that the lattice parameters for VO_x are derived from electron diffraction images, and are consequently less accurate, the agreement between $b(VO_x)$ and $c(V_4O_9)$ on the one hand, and between $a(VO_x)$ and $a(V_4O_9)$ and/or $b(V_4O_9)$ on the other, is good. The question arises whether the third parameter is 8·235 Å $[=b(V_4O_9)]$ or twice that distance $[=c(VO_x)]$. $c(VO_x)$ has been reported to be parallel to $c(V_2O_5)$ and perpendicular to the plane formed by $a(VO_x)$ and $b(VO_x)$ (Tilley & Hyde, 1970). From the X-ray diffraction experiments on phase *Q* (Colpaert, 1972) it has been concluded that the distance between the net planes, parallel to the V_2O_5 (001) plane, is 16·48 Å.

The diffraction spots on our oscillation photographs can indeed only be indexed taking into account a third lattice parameter of approximately 16·48 Å. V_4O_9, consequently, is orthorhombic and not tetragonal, as first proposed by Théobald, Cabala & Bernard (1969). The X-ray diffraction spectrum given by these authors can be indexed with $a=8·235$, $b=10·32$, $c=16·47$ Å.

5. *Density*

According to Théobald, Cabala & Bernard (1969), the density of V_4O_9 is 3·25 g cm^{-3}. This value is very low compared to those of other vanadium oxides (V_2O_5: 3·377; V_3O_7: 3·58; V_6O_{13}: 3·92 and VO_2: 4·67 g cm^{-3}). The unit cell of V_2O_5 contains two formula units (V_4O_{10}). The calculated density of a V_2O_5 lattice from which one O atom per unit cell is removed would be 3·228. The composition of such a hypothetical superstructure is V_4O_9. This calculated density agrees well with the experimentally determined density of V_4O_9.

6. *Considerations about the preparation methods*

The structure of the vanadium oxides consists of O polyhedra surrounding V atoms. The transition of V_2O_5 into most of the lower oxides involves a rearrangement of these O polyhedra, which requires rather high temperatures (>400 °C). V_2O_5 can be reduced in vacuum already at 100°C. At this temperature a sevenfold superstructure is formed (Tilley & Hyde, 1970) and no rearrangement of polyhedra occurs. Tilley & Hyde obtained VO_x by thermal treatment of V_2O_5 in vacuum at temperatures as low as 150°C. This temperature seems to be too low to produce a rearrangement of O polyhedra, and the structure of this phase thus should very nearly be that of V_2O_5.

III. The structure of V_4O_9

The observation that V_4O_9 grows topotaxically on V_2O_5 single crystals, together with considerations concerning its growth conditions and density indicate that V_4O_9 could be a (slightly deformed) superstructure of V_2O_5. The purpose of this paper is to propose such a structure.

Consider the primitive unit mesh of the reciprocal lattice of the topotaxic V_4O_9 (Fig. 2). The unit vectors of this primitive unit mesh [$\bar{a}^*(p\text{-}V_4O_9)$ and $\bar{b}^*(p\text{-}V_4O_9)$] are shown in Fig. 3, together with reciprocal unit vectors of the V_2O_5 substrate lattice. Fig. 4 shows the corresponding unit vectors in the direct lattices.

The unit vectors $\bar{a}(p\text{-}V_4O_9)$ and $\bar{b}(p\text{-}V_4O_9)$ are equal in length, approximately 6·4 Å (corresponding to d_{110} in VO_x). The angle between $\bar{b}(V_2O_5)$ and $\bar{b}(p\text{-}V_4O_9)$ is $\alpha/2=2°$. The angle between $\bar{b}(p\text{-}V_4O_9)$ and $\bar{a}(p\text{-}V_4O_9)$ is approximately 104°, the angle between $\bar{a}(p\text{-}V_4O_9)$ and $\bar{a}(V_2O_5)$, consequently, is 12°.

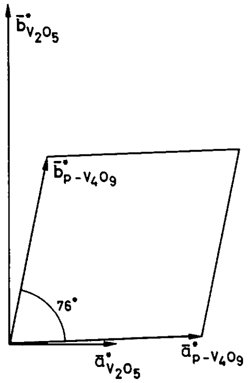

Fig. 3. Reciprocal unit mesh of the V_4O_9(001) surface, together with the corresponding V_2O_5(001) reciprocal unit mesh.

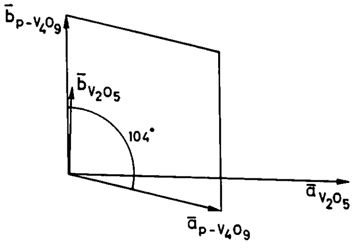

Fig. 4. Direct unit mesh of the V_4O_9(001) surface, together with the corresponding V_2O_5(001) direct unit mesh.

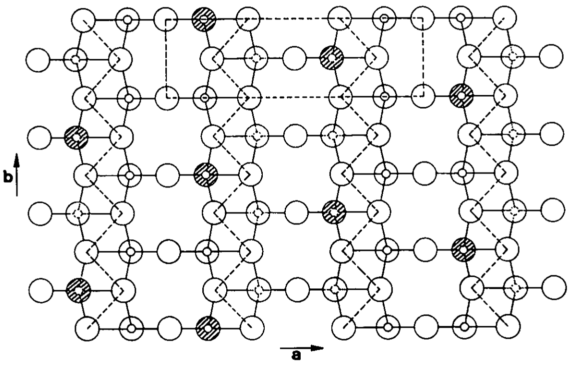

Fig. 5. Projection of the V_2O_5 structure on the *ab* plane [(001) plane], with one tenth of the O atoms removed.

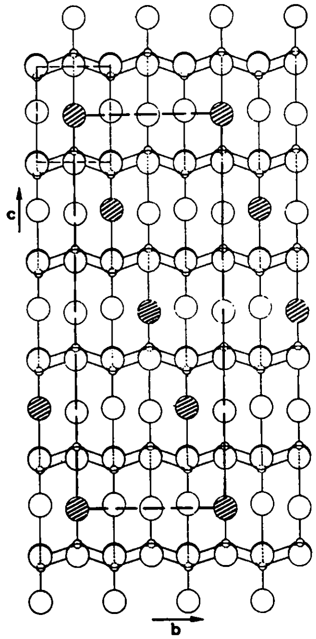

Fig. 6. Projection of the superstructure on the *bc* plane [(100) plane].

Consider now the projection of the V_2O_5 structure on the *ab* plane and suppose that one tenth of the O atoms are removed, in the manner indicated in Fig. 5. The unit mesh in this hypothetical superstructure would have one unit vector parallel to $\bar{b}(V_2O_5)$ of length $2|\bar{b}(V_2O_5)|=7{\cdot}126$ Å. The second unit vector would have a length of 6·024 Å and would include an angle of 17° with $\bar{a}(V_2O_5)$; the angle between the two unit vectors in this model would consequently be 107°. Fig. 6 shows the projection of this superstructure on the *bc* plane. The unit vector in the third direction would be $4|\bar{c}(V_2O_5)|=17{\cdot}48$ Å.

The differences between the characteristics of this superstructure and those of V_4O_9 are small and can easily be explained by minor distortions. A driving force for this distortion seems to be a repulsive action between the O vacancies: in the *ab* plane of the un-

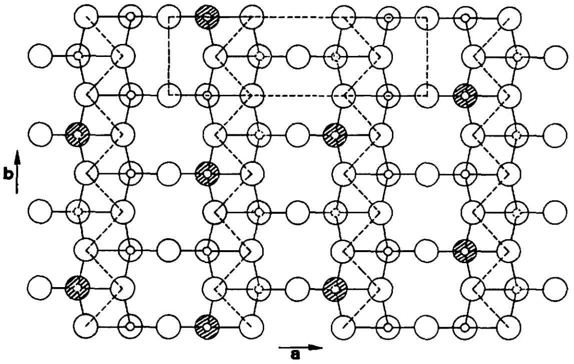

Fig. 7. Irregularity in the sequence of oxygen vacancies gives rise to typical twin formation.

distorted superstructure, the distances between neighbouring vacancies would be 6·024 and 7·126 Å, while both would become equal to 6·4 Å in their equilibrium position. Fig. 7 shows that a simple irregularity in the sequence of O vacancies explains the typical formation of twins.

Other models are possible in which the O vacancies are located on other sites but with the same arrangement. Because it has been shown (Sachtler & de Boer, 1964; Tarama, Teramishi, Yoshida & Tamura, 1964) that the vanadyl O atom is the most reactive, we prefer the model in which vanadyl O atoms are removed periodically.

The formation of superstructures also occurs in other metal–oxygen systems of which the different phases TiO_x for $0·7<x<1·3$ are examples. The basic structure of all these oxides is the NaCl structure. Quenching from 1500 °C results in a random distribution of Ti and O vacancies in a NaCl structure. Bakeout at relatively low temperatures (up to 950 °C) results in an ordering of the vacancies. The arrangement of the Ti and O vacancies can be rather complicated and depends on the composition (Collongues, 1971). A first indication for the existence of superstructures related to the V_2O_5 structure was given by Tilley & Hyde (1970). The results of the present work are taken as an indication that V_4O_9 is another slightly distorted superstructure of V_2O_5.

IV. Summary

It has been shown that the previously described vanadium oxide phases Q and VO_x are both identical with V_4O_9 (Théobald, Cabala & Bernard, 1969). From X-ray oscillation photographs it can be concluded that the structure of V_4O_9 is orthorhombic. The X-ray diffraction spectrum can be indexed with $a=8·235$, $b=10·32$, $c=16·47$ Å. A model for the structure of V_4O_9 based on a superstructure of V_2O_5 is proposed. This model is in agreement with the results of the X-ray oscillation diagrams and with the extremely low density of this material. It also accounts for the topotaxic growth of V_4O_9 on V_2O_5, its formation at low temperatures and the typical appearance of twins.

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