Contributions to the Chemistry of Molybdenum and Tungsten, IX

Some Aspects of the Structure of WO₃ and a Contribution to the Understanding of the so-called “Shear Structures”

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Combination of forms of WO₃, Periodic Bond Chain (PBC) Vector Method, Crystallographic Shear (CS) Structures

By using the Periodic Bond Chain Vector method a newly prepared combination of forms of highly stoichiometric WO₃ is discussed. Through the consideration of the features of the structure it can be explained, why the observed faces are built. From characteristics of the structure an improved understanding of the origin of so called shear structures of the ReO₃ type family could be derived.

Lasting interest in preparing and understanding material of the substoichiometric region of WO₃, as well as of the series M₁₋ₓO₃ (M = Mo, W) and the recent determination of a new combination of forms (Tracht) of highly stoichiometric WO₃ caused the discussion of WO₃ according to the Periodic Bond Chain (PBC)-vector method of HARTMAN and PERDOK.

Experimental Background

The crystal structure of the monoclinic room temperature modification of WO₃ was lastly determined by LOOPSTRA and BOLDRINI by neutron diffraction and refined by LOOPSTRA and RIETVELD. The structure can be described — as already known before — as a distorted ReO₃-structure with corner-sharing WO₆-octahedra. The projection of the unit cell along [010] is shown in Fig. 1. From the eight octahedra four are related by symmetry. The octahedra are notably distorted. The distortion consists firstly of a rotation of the chains of octahedra around [010], which leaves the symmetry related chains in the slice parallel to each other, compared with the ReO₃-structure. The distortion

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Fig. 1. Projection of WO₃ along [010]. Only the half cell along the b-axis is shown. Small circles are W atoms, larger circles O atoms. Atoms with broken lines above, dotted below the plane of drawing. Full lined atoms are approximately in the plane of the paper.

* In the nomenclature of the PBC-method, dhkl is used for the representation of the period with which the surface energy is repeated (or nearly so in the case of pseudo periods). In the case of layer growth, dhkl is the thickness of the elementary growth layer.
consists further of a twodimensional displacement of the tungsten atoms from the centre of the octahedra. Both irregularities of the coordination polyhedron so fit the model given by Megaw.

In terms of chemical bonding, WO₃ consists of endless chains of tungsten-oxygen bonds of alternating length in two directions ([001] and [010]) while the bonds along [100] differ less in length. The values of these different bond lengths calculated after the data of Loopstra and Rietveld are given in Table I.

Table I. Tungsten-Oxygen bond lengths (Å) of WO₃ calculated after the data of Loopstra and Rietveld. Figures in parenthesis give the standard deviations related to the last digit.

<table>
<thead>
<tr>
<th>Chemical bond lengths</th>
<th>Along [100]</th>
<th>( \frac{1}{2} ) [100]</th>
<th>( \frac{1}{2} ) [010]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[001]</td>
<td>1.931(15)</td>
<td>1.840(15)</td>
<td>1.733(9)</td>
</tr>
<tr>
<td>[002]</td>
<td>2.093(14)</td>
<td>1.743(15)</td>
<td>2.175(9)</td>
</tr>
<tr>
<td>[003]</td>
<td>2.119(15)</td>
<td>1.738(9)</td>
<td>2.178(9)</td>
</tr>
</tbody>
</table>

While most papers, dealing with WO₃ single crystals describe plates with (001) as basal plane, less claim to have plates with (010). Only Tanisaki and Kleber, Hähnert and Müller had crystals with octahedral habits. Without giving any measured angles, planes of {111} were believed to occur. Kleber et al. claimed to have crystals showing {111} and {112} beside {001} and {100}. Using a new kind of preparation, Schröder and Felser recently obtained the following combinations of forms. Most of the crystals showed {112} - {112} - {001}, often {112} - {112}, seldom {001} - {100} - {112}, there was also a cleavage plane belonging to {012} as proved by goniometric measurements. Besides the well known (100)-microdomains a macroscopic twin along (110) was found.

Monoclinic WO₃ crystallizes in the centro-symmetric space group P 2₁/n. As Schröder and Felser observed, both, growth spirals on {112} elongated along [110] and growth steps on {001} and {100} occur. It seems therefore that these faces grew according to a layer growth mechanism. The question arises as to which habit may be expected.

Theoretical Background

The relation between the morphology of a crystal, its lattice dimensions and its space group is expressed by the law of Donnay and Harker, according to which the importance of a crystal face decreases with decreasing interplanar spacing \( d_{hkl} \), the effect of screw axes and glide planes taken into account. In the present case this latter effect introduces halving of lattice \( d_{hkl} \) values for \( (h0l) \) when \( h + l = 2n + 1 \) and for \( (0kl) \) when \( k = 2n + 1 \). Noting that \( 1/2 d_{hkl} = d_{3h, 2k, 2l} \), we obtain the following sequence of decreasing \( d_{hkl} \) values:

\[
\begin{align*}
011, & \ 101, 110, \ T11, 111, 002, 020, 200, 012, 021, 120, 210, \ T12, 112, \ T21, 121, \ T21, 211, \ldots \\
\end{align*}
\]

This sequence is violated by the experimental observations. Donnay and Donnay gave an extension of the law of Donnay and Harker by pointing out that pseudosymmetry may cause additional halving of some \( d_{hkl} \) values. The WO₃ structure shows pronounced pseudosymmetry in its similarity to the ReO₃ structure. The pseudo unit cell of WO₃ has dimensions equal to about half the real axial lengths. This involves halving of \( d_{hkl} \) whenever \( h, k \) or \( l \) are uneven. The final order according to Donnay and Donnay now becomes:

\[
\begin{align*}
002, & \ 020, 200, 022, \ 002, 202, 220, \ 222, 222, \ldots \\
\end{align*}
\]

According to this series the most prominent face should be (001) as it has been often observed, but the dominating (T12) and (112) rank as numbers 21 and 22, respectively. In order to find an explanation for the occurrence of these faces the Periodic Bond Chain (PBC) method is applied. According to the underlying theory, the morphology is governed by a set of uninterrupted chains of strong bonds (PBC's). The strong bonds are bonds in the first coordination sphere formed during the crystallization process. It is then possible to distinguish three categories of faces:

- F faces (flat faces), where two or more PBC's in different directions occur within a slice \( d_{hkl} \);
- S faces (stepped faces), where only one PBC occurs in a layer \( d_{hkl} \);
- K faces (kinked faces), where in a layer \( d_{hkl} \) no PBC occurs.

F faces are the most prominent faces and they grow according to a layer growth mechanism. K faces grow fast as no nucleation process is needed. Usually they do not appear, but some may become important when adsorption of foreign particles plays a role. Often the particles are strongly adsorbed at kink sites, thereby decreasing the growth rate of K faces, notably those with a high kink density and therefore a large \( d_{hkl} \) value. S faces have an intermediate position.

Discussion of the Combination of Forms of WO₃

If, for the moment, we consider the building units in WO₃ to be the W and O atoms, the strong bonds are the W – O bonds in the distorted octahedra.
PBC's occur in the directions [100], [010], and [001] and the forms {100}, {010} and {001} are F forms. As to the relative importance of faces the hypothesis is made in the PBC theory, that the importance decreases with increasing attachment energy. This attachment energy is defined as the energy released per molecule when a new slice $d_{hkl}$ is deposited onto the crystal face. In other words, the attachment energy is the interaction energy between two neighbouring slices per molecule. In the present case the following bonds are formed between adjacent slices (per 4 molecules WO$_3$):

- for $d_{200}$ two 1.931 and two 1.946 Å bonds
- for $d_{020}$ two 2.093 and two 2.119 Å rings
- for $d_{002}$ two 2.175 and two 2.178 Å bonds.

If we assume that the formation of a shorter bond corresponds to a higher amount of energy released, the order of decreasing importance is: (001), (010), (100), the same is found from the law of DONNAY and DONNAY. This order is not affected when other building units are considered.

It is more likely that growth takes place by molecules instead of atoms. NORMAN and STALEY showed most recently by mass spectroscopic measurements with a Knudsen cell, that at the WO$_3$ crystal growth conditions the vapour contains almost exclusively the species W$_3$O$_9$ and W$_4$O$_{12}$ besides few monomer, dimer and pentamer. The dominating tri- and tetramer species are regarded to consist of a six and eight membered tungsten-oxygen ring-molecule, respectively, which was proved for W$_3$O$_9$ by vapor electron diffraction experiments by HARGITTAI et al.

Under this perspective, other PBC's can be constructed, namely in the directions (110), (101), (10T) and (011). These have a zigzag structure and determine other F forms: {110}, {101}, {01T}, {011}, {111} and {T11}. However, if we consider the broken bonds at the surface of, for example, (101), it is found that exactly the same kind of bonds would be broken if the surface were displaced over a distance $1/2 d_{101}$. This means that almost the same surface energy is repeated at $d_{002}$. The same holds for the other faces just mentioned. Because of in the halved slices the PBC's cannot occur, the forms {110}, {01T}, {101} and {011} are to be considered as S forms and {111} and {T11} as K forms.

As a consequence also {112} and {T12} are K forms. A projection along [1T0] shows that the slice $d_{112}$ can have on its surface six broken long bonds (two 2.175, two 2.178, one 2.119 and one 2.093 Å bonds) and two short bonds (one 1.946 and one 1.931 Å bond) per 4 molecules WO$_3$.

These are the longest bonds in the structure, so the surface energy is relatively low. For these faces no halving of the period $d_{hkl}$ occurs. The appearance of (112) and (T12) can now be explained by chemisorption of O$_2$ at the sites of these long bonds.* The longest out of these bonds are also broken on the surface of (001), but here only four broken bonds occur instead of six with (112) and (T12). This is one reason that the effect of adsorption on the latter faces must be larger and their growth rates diminished, eventually to such an extent that no other forms can persist. The second reason is that the adsorption on K faces is presumably stronger than on F faces, because K faces have a much higher electrostatic field normal to their surface than F faces. The species W$_3$O$_9$ and W$_4$O$_{12}$ cannot be responsible for the appearance of (112), since these molecules are also present at lower O$_2$ concentrations, where the form {112} has not been observed.

The importance of the longest bonds also explains the absence of forms like {211} and {121}. On the surface of (211) faces only four long broken bonds occur (2.178, 2.175, 2.119 and 2.093 Å) with four short broken bonds (two 1.946 and two 1.931 Å bonds), so there are only four adsorption sites for O$_2$. Similar arguments hold for (121).

The weakness of the longest bonds is also responsible for the cleavage along (012). Here the same long bonds are involved as is seen from Fig. 2.

**Crystalllographic Shear Structures**

**of the ReO$_4$ Type Family**

On the basis of the preceding results, an attempt is made to get a better understanding of the mechanism through which so-called crystalllographic shear (CS) structures are built. This part deals only with those structures of molybdenum and tungsten oxides which belong to the homologous series $M_nO_{3n-1}$ and $M_nO_{3n-2}$.

ANDERSON and HYDE developed the fundamental scheme. They reduced the structure of WO$_3$ *KLEBER et al. received from their crystal growing with transport reaction, octahedral crystals at same temperatures probably also due to chemisorption of halogen.
and an analogous, but hypothetical one of MoO₃ to a theoretical structure, that is a regular as the ReO₃ structure. Concerning the series MₙO₃ₙ₋₁, they considered \{120\}_R** planes of this structure. These planes obey the stoichiometry MO₃ (A planes) and O₂ (B planes). In the hypothetical structure they have the sequence ... ABABAB ... After a certain number of AB sequence (each giving a n = 1 step to the resulting shear (CS) structure) a B plane is missing. In that way the shear plane is created at this point of the sequence. For the series MₙO₃ₙ₋₂ the \{130\}_R planes are considered, having the stoichiometry MO (A planes) and O₂ (B planes). Again the sequence is ... ABABAB ... Again a B plane is missing, thus producing the shear plane. But now the two neighbouring A planes “amalgamate”, giving an A₂-plane which leads to the observed stoichiometry, i.e. W₂0O₅₈. This structure is shown in Fig. 3.

This scheme neglects one important fact, namely the difference between the elements W (Mo) and Re. WO₃ does not build such a regular structure as ReO₃ does. From the results obtained in the preceding discussion it is attempted to understand in an atomistic view which part of the parent WO₃ structure is going on to become the structural sheet (perpendicular to the b-axis) in, say W₂0O₅₈.

Up to now, absolute stoichiometric WO₃ has not yet been described. The highest composition due to BERAK and SIENKO has been W₀₂.₉₉₉₉₉₉₅. We assume, that exact WO₃ can be prepared (under O₃ pressure?) and that it has a structure as that one given by LOOPSTRA and BOLDRINI. Obviously this compound is not thermodynamically unstable. The reason why WO₃ in the region of its substoichiometry exhibits such a spectrum of effects, can be best understood by first summing up some experimental results known hitherto.

1) SPYRIDELIS, DELAVIGNETTE and AMELINCKX first investigated domains, having their traces \((001)\) of the WO₃ lattice \((001)\)-domains) in crystals of substoichiometric tungsten trioxide. They showed that these domains consist of flakes (fringes) of noticeable lower oxygen content. ALLPRESS and GADO investigated crystals with an overall composition of about W₀₂.₉₉₉₉ (equal to about W₂₀O₅₈) and proved from the slightly different spacings between the fringes of the planar defects, that they consist of flakes of oxides of the series WₙO₃ₙ₋₂. The authors showed to have detected hitherto unknown members of this series \(n = 14 - 28\). SCHRÖDER and FELSER showed, that their crystals with an oxygen content higher then W₀₂.₉₉₉₉ do not show these domains of substoichiometry. The same results obtained ALLPRESS, TILLEY and SIENKO who observed in crystals of the composition W₂₀O₅₈ only rarely \{120\}_R planar defects.

2) VAN LANDUYT and AMELINCKX first explained the nature of a second kind of fringes, already known before. They worked out, that the long W...O₂ distances \((2.175, 2.178\) Å) in the structure of WO₃ have to be considered as electric dipoles. The explanation of the nature of these \((100)\) domains is shown in Fig. 4. If a neighbouring unit cell in \([100]\) direction is not a translatorial one, but a twin related one, then repulsive forces on the border of both will occur from the...
Fig. 4. Model for the explanation of domain walls parallel (100). (The drawing is taken from ref. 21.)

parallel ordering of the dipole chains. SCHRODER and FELSER 2 could confirm this interpretation from their results. Their crystals, which did not show the (001) domains, always showed (100) domains.

The origin of the (100) twins must be sought in the pseudosymmetry of the structure. Along [100] the difference between the bond lengths is smallest, along [001] it is largest. The strain caused by an error is therefore most easily accommodated in the [100] direction. As in fact the displacements are rather small, (100) twins are to be expected. For (001) twins the displacements and the associated strains are much larger, so that they do not occur in highly stoichiometric WO3.

A similar argument holds for the macroscopical, merohedral growth twin which has been found by SCHRODER and FELSER 2 and which is denoted being a (110) twin (110) domains have been observed among others by SAWADA and DANIELSON 22 and most recently by BERAK and SLENKO 17. With an optical goniometer a re-entrant angle of about 2° on (001) was measured, which agrees well with the calculated value of 1° 16'.

The dimensions of the unit cell and the idealized structure would permit (110) as well as (011), (101) and (001) twins. The preference for (110) twins is due to the fact that in the [100] and the [010] directions the differences in lengths between the bonds are smallest. Moreover in a slice d002 two oxygen atoms can be found for which the difference in x and y coordinates is 0.4950 and 0.5000, respectively. Thus, a reflection of the structure on (110) would leave these atoms virtually in place. For the other faces the differences are always larger.

Hence, among the possible twin planes (110) is associated with the smallest distortions.

The consequent discussion along these lines, together with the preceding results gives the following picture: In Fig. 5 two unit cells of monoclinic WO3 are shown. As may be recognized easily, dipole chains along [001] * have only other antiparallel chains as neighbors if the two cells are related by translation. Chains along [010] in the slice d002 have always antiparallel chains as neighbors, while the slices are stacked in such way, that a parallel sequence of [010] chains results. This parallelism causes a certain amount of repulsive forces along [001] between the slices d002 which weakens the structure in this direction and which enlarges the tendency that (001) plate crystals grow.

This repulsion can be considered as a result of a tendency of O2 atoms to prefer a higher degree of 7-bonding with the tungsten atom to which it is bonded mainly, instead of taking part in a higher amount of bonding with a second tungsten atom. This is confirmed by the work of LOOPSTRA and RIETVELD 5 according to which the long W...O2 bonds are 2.175 and 2.178 Å, while the comparable long W...Oy bonds are only 2.093 and 2.119 Å. As a consequence the (CS)-structure oxides of the ReO3-type family, e.g. W2O5, have to be considered as being with their dominating structural sheet (perpendicular to its b-axis), formerly d002 slices of the WO3 structure.

* From here also called [001]- and [010]-chains.
All structures of these compounds are built of two-dimensional sheets (cf. Fig. 3) with the perpendicular extension of only one metal-oxygen octahedron. Unfortunately no experimental data exist about the distortion of these octahedra, neither from those which are WO$_3$ structure like with four common corners with neighbouring octahedra, nor from those which share edges (cf. Fig. 3).

In the following, a proposal is made about the relationship of the bondings of the same atoms of a coordination polyhedron in WO$_3$ and one (not affected by loss of oxygen) in, e. g. W$_{20}$O$_{58}$. As the formation of CS-structures needs temperatures of at least several hundreds degrees centigrade and as it can be assumed that through thermal motion the repulsion of the parallel [010] chains increase, it is believed, that there is a further weakening of the longer W—O-distances of the structure along [001] under these conditions of temperature. It is assumed, that this is a necessary precondition to enable the rearrangements of the structure for changing from the WO$_3$ lattice to one of a CS-structure.

According to the proposal concerning the relationships of same atoms in both structures, it is expected, that the bonding is as shown schematically in Fig. 6, since a linear O=W=O arrangement has never been reported. Thus only a slight rearrangement of the electron distribution (or a 90° rotation of the octahedra around [010]?) has to take place, as Fig. 6 shows, to give the arrangement of the WO$_3$ structure like parts of, say W$_{20}$O$_{58}$. During the reduction, O atoms are removed from such planes, which leads to the series M$_n$O$_{3n-1}$ and M$_n$O$_{3n-2}$ as described at the beginning of this chapter. The way in which this may take place has been described in detail very recently by Allpress, Tilley and Sienko. Due to the deduced view, O$_x$ and O$_y$ type atoms are those which are removed, or, were not present in the starting WO$_3$ material which has widely been used.

Which of those mentioned two types of oxygen atoms most probably could already be absent? As it has been shown in the preceding discussion, the fastest growth of WO$_3$ crystals takes place in the [100] direction. It is a well known consequence, that in such direction the probability for errors is highest. The recent results of Allpress, Tilley and Sienko are proving this in a striking way, because they observed most of their planar defects lying along [120], only very few parallel to [120], [210] and [210]. Parallel to [120], lies (210) and along this plane only O$_x$-atoms of the WO$_3$ structure have to be removed to produce the crystallographic shear.

So it can be concluded, that for the description of the CS-structure of the ReO$_3$-family in the case of tungsten (the case of molybdenum is under investigation at present) the model of this structures is not the ReO$_3$ structure but the structural slice d$_{002}$ of WO$_3$.

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2 Cf. reference 1.

Kinetics and Mechanism of Os(VIII) Catalysed Oxidation of Mandelate Ion by Alkaline Ferricyanide

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The kinetics of the reaction between alkaline ferricyanide and mandelic acid catalysed by [Os(VIII)] has been studied. The rate of ferricyanide disappearance was found to be proportional to the concentration of mandelate ion and Os(VIII), but independent of the concentration of ferricyanide. Within a limited concentration range of hydroxyl ion [OH$^{-}\$] < 0.25 M the rate varies directly as the [OH$^{-}\$]. Effects of SO$_4^{2-}$, NO$_3^{-}$ and temperature on the rate were studied. $\Delta E$, $PZ$, $\Delta S^*$ etc. were evaluated. Mechanism of oxidation of mandelic acid based on the formation of Os(VIII) acid anion complex is suggested.

Kinetic studies on oxidation of a variety of substances, both organic and inorganic by ferricyanide have been undertaken by many workers. Unless a catalyst is employed these reactions are either extremely slow or do not proceed at all. The most widely investigated catalyst is Os(VIII).

Among several compounds the kinetics of oxidation of 3-mercaptopropionic acid$^1$, 2-mercapto ethanol$^2$, thioacetamide$^3$, ascobic acid, thiourea, acetaldehyde$^4$, have been investigated.

A review of the literature shows that oxidation of $\alpha$-hydroxy acids by alkaline ferricyanide has not received much attention. The present report deals with the results on the oxidation of mandelic acid by alkaline ferricyanide catalysed by Os(VIII).

Experimental

Material: OsO$_4$ (Johnson & Mathey), and potassium ferricyanide (Anala 'R' Sample), mandelic acid (Mallinckrodt) were used. All other chemicals were chemically pure.

Catalyst: It was obtained by dissolving known weight of OsO$_4$ in KOH solution [0.05 M].

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Reaction mixture containing the requisite quantities of mandelic acid, NaOH, OsO$_4$ were prepared in the reaction vessel. The reaction mixture and potassium ferricyanide solution were thermostated for about twenty min. to attain experimental temp. 35 $^\circ$C. A known volume of ferricyanide was then transferred to the reaction mixture and aliquots were removed from time to time and analysed for unconsument ferricyanide within the wave length range of 400—450 m$\mu$. Variations of the concentration of ferricyanide were well within the range of Beer’s law ($1.6 \times 10^{-3}$ M — $5.0 \times 10^{-3}$ M). No absorption was evident due to other species.

Results

Since the rate laws are not affected by the presence or absence of oxygen no attempt was made to remove oxygen from the reaction mixture. [Substrate] $\gg$ [Fe(CN)$_6^{3-}$]. So as to prevent secondary oxidation of products. Zero order rate constants ($k_0$ s) were found to be independent of the initial concentration of ferricyanide (Table 1). The reaction was found to be of first order with respect to each [mandelate] and [Os(III)]. The values $\frac{k_0}{[\text{mandelate}]}$ (Table 2) and $\frac{k_0}{[\text{Os(VIII)}]}$ (Table 3) were found to be fairly