ROBERTSON, J. M. & WOODWARD, I. (1937). *J. Chem. Soc.* p. 219.
RUNDLE, R. E. & PARASOL, M. (1952). *J. Chem. Phys.* **20**, 1487.
SHAHAT, M. (1951). *Acta Cryst.* **5**, 763.
VAND, V. (1951). *Acta Cryst.* **4**, 285.
YAMADA, S. (1951). *Bull. Chem. Soc. Japan*, **24**, 125.

Acta Cryst. (1953). **6**, 495

Structures of the ReO_3-type with Recurrent Dislocations of Atoms: 'Homologous Series' of Molybdenum and Tungsten Oxides*

BY ARNE MAGNÉLI

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

(*Received* 24 *January* 1953)

The geometrical properties of structures of the ReO_3-type showing recurrent dislocations of atoms, analogous to those present in Mo_8O_{23}, Mo_9O_{26} and $W_{20}O_{58}$, are discussed. Two of the hypothetical atomic arrangements thus derived have been found to correspond to recently prepared molybdenum tungsten oxides $(Mo,W)_{10}O_{29}$ and $(Mo,W)_{11}O_{32}$. These compounds and the aforementioned molybdenum oxides are members of a 'homologous series', Me_nO_{3n-1}, based on a common structural principle. There is almost complete agreement between the experimentally derived structures of these homologues and the corresponding ideal structures. The same is also true for $W_{20}O_{58}$, the only hitherto known representative of the series Me_nO_{3n-2}.

Introduction

Investigations of molybdenum and tungsten oxides with an average valency of the metal atoms slightly less than six, namely Mo_8O_{23}, Mo_9O_{26} and $W_{20}O_{58}$, have shown that the crystal structures of these compounds are mutually closely related and based on structures of the ReO_3-type (*Strukturbericht*, 1937) containing dislocations of the atoms, suddenly occurring after long periods (Magnéli, 1948, 1950*a*, *b*). A geometrical discussion of hypothetical structures analogous to those derived for these oxides has proved to be valuable when investigating a number of double oxides of molybdenum and tungsten (Magnéli, 1952; Blomberg, Kihlborg & Magnéli, 1953) and will be described here. A comparison will be given between the crystal structures of the known oxides of this type and the corresponding hypothetical structures.

Structural principles of Mo_8O_{23}, Mo_9O_{26} and $W_{20}O_{58}$

The crystal structures of these oxides may be described as built up of metal–oxygen octahedra joined by corners to form blocks of the ReO_3-type, which extend infinitely through the crystals in two dimensions and have a finite, characteristic width in a third direction. The blocks are mutually joined along folded planes by octahedra having edges in common. These planes correspond to the recurrent dislocations of atoms occurring in the ReO_3-type structure.

The structures of Mo_8O_{23} and Mo_9O_{26} differ only in respect of the finite width of the ReO_3-type blocks, which extend through eight and nine MoO_6 octahedra respectively. The appearance of the planes joining the blocks is the same in both oxides and is characterized by the recurrent occurrence of groups of four MoO_6 octahedra joined by sharing edges (Figs. 1(*d*), 4(*a*), (*b*)). There is a regular, alternating displacement of the metal atoms in the octahedra, parallel to the *b* axes of the monoclinic unit cells (normal to the plane of the figures). The metal atoms thus form puckered layers parallel to the *ac* plane. There is a marked lengthening of the MoO_6 octahedra perpendicularly to this plane. The molybdenum atoms of the quadruplets of octahedra sharing edges are situated in planes characteristically tilted. The considerable distortion of the MoO_6 octahedra may suggest that the molybdenum atoms can be considered as co-ordinating five oxygen atoms in a square-pyramidal arrangement. For the following discussion, however, the simplified picture of distorted MoO_6 octahedra is more convenient.

The dislocation planes occurring in $W_{20}O_{58}$ are of a somewhat different appearance from those present in the molybdenum oxides, in showing groups of six metal–oxygen octahedra joined by sharing edges (Fig. 1(*e*)). The finite extension of the ReO_3-type blocks in this structure amounts to twenty octahedra. The metal atom layers are not puckered.

---

* A survey of this investigation was presented at the meeting of the American Crystallographic Association in Camp Tamiment, Pa., June 1952.

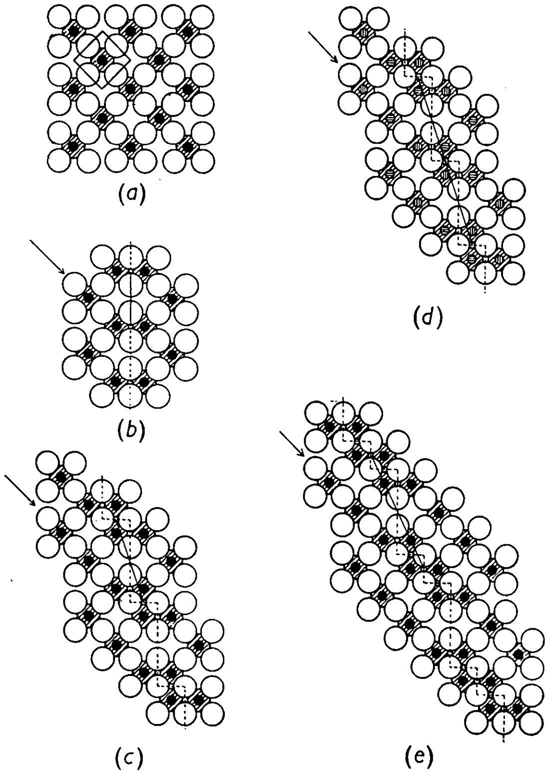

Fig. 1. (a) The ReO_3-type structure. The Me atoms (small, black circles) are co-ordinated with six oxygen atoms (large circles) to form MeO_6 octahedra, which are joined by sharing corners. The oxygen atoms nearest to the observer are omitted to show the underlying metal atoms. The extension of one unit cell is indicated. (b) The border region of the ReO_3-type blocks of structures Me_nO_{3n} ($m = 1$), built up of regular MeO_6 octahedra. The projection of the contour plane of the blocks is indicated by a broken line and the direction of characteristic finite extension of the blocks by an arrow. (c) The border region of structures Me_nO_{3n-1} ($m = 2$) with non-puckered metal atom layers. (d) The corresponding arrangement for lattices Me_nO_{3n-1} with metal-atom layers puckered in the same way as those of Mo_8O_{23} and Mo_9O_{26}. The displacements of the metal atoms are indicated by the vertical and horizontal shading of the small circles. (e) The border region of structures Me_nO_{3n-2} ($m = 3$).

Hypothetical structures

It is obvious that a large number of structures can be formed by combining metal–oxygen octahedra (MeO_6 octahedra) in a similar manner to those present in the molybdenum and tungsten oxides described in the preceding paragraphs. However, the investigation was essentially restricted to discussions of the effects in atomic arrangements analogous to that of $W_{20}O_{58}$ of varying (a) the finite width of the ReO_3-type blocks (n MeO_6 octahedra) and (b) the number of pairs of octahedra participating in the mutual joining of these blocks (m pairs of MeO_6 octahedra). Moreover, the geometrical properties of 'puckered' structures analogous to those of Mo_8O_{23} and Mo_9O_{26} ($m = 2$) were studied as a function of n. The value of m was considered to be the fundamental variable as it determines the shape of the border planes of the ReO_3-type blocks and defines two of the lattice constants of the structures (parallel to this plane). It was thus natural to classify all the structures considered according to m in groups or series, the various members of which differ only in respect of the finite width of the blocks. It seems reasonable to characterize these series, expressible by general formulae and built on common structural principles, as *homologous series*. In the following the geometrical properties of some of these series will be discussed.

The Me_nO_{3n} *series*

When the rearrangement of the ReO_3-type structure is restricted to the introduction of groups of two MeO_6 octahedra sharing edges ($m = 1$), as illustrated in Fig. 1(*b*), every oxygen atom will still belong to two octahedra and the ratio of metal atoms to oxygen atoms will remain 1:3. The unit-cell content will thus correspond to the formula Me_nO_{3n} ($n \geq 2$). The symmetry of the arrangement will be $P2/m$ for n even and $Pmmm$ for n odd. No representatives of this series are known and as it is to some extent divergent from the other ones, it will be disregarded in what follows.

The Me_nO_{3n-1} *series*

(*a*) *Non-puckered metal atom layers.*—The appearance of the border regions when four MeO_6 octahedra are participating in the joining of the blocks ($m = 2$) is illustrated in Fig. 1(*c*). Two of the oxygen atoms in these groups belong to three octahedra, while all the other oxygen atoms of the structure are common to two octahedra. The general formula of the series will thus be Me_nO_{3n-1} ($n \geq 4$). The symmetry of the arrangement is $P2/m$.

(*b*) *Puckered metal atom layers.*—If the metal atoms are assumed to form puckered layers (Fig. 1(*d*)), as in Mo_8O_{23} and Mo_9O_{26}, this will change the symmetry of the structure to $P2/a$ and double the unit cell, and thus give the cell content $2\,Me_nO_{3n-1}$. Some doubt may exist which minimum value of n ought to be assigned to such an atomic arrangement.

General series

If groups of $2m$ MeO_6 octahedra with edges in common (m pairs of octahedra) are taking part in the joining of the blocks (cf. Fig. 1(*e*), where $m = 3$) structures of the composition Me_nO_{3n-m+1} and of symmetry $P2/m$ will result (unpuckered metal atom layers).

When calculating unit-cell dimensions and atomic positions of the various structures, combinations of regular MeO_6 octahedra may be considered, as was actually done in some previous articles (Magnéli, 1948, 1952). This, however, represents a rather rough approximation, as the close approach of the high-valent metal atoms of the octahedra joined by sharing edges must imply considerable repulsive forces between these atoms, leading to lengthening of the interatomic distances and a corresponding distortion of the MeO_6 octahedra involved. The various parameters of the hypothetical structures were thus calculated assuming (a) that the metal-atom positions within the blocks are arranged as in an ideal ReO_3-type structure with the interatomic spacing equal to d (or occasionally rearranged to form puckered layers) and (b) that the distances between the metal atoms of octahedra joined by edges is e, exceeding the distance of $d/\sqrt{2}$ valid for regular octahedra. In the calculations the latter condition was introduced by a parameter δ (cf. Fig. 2) related to d and e by the equation

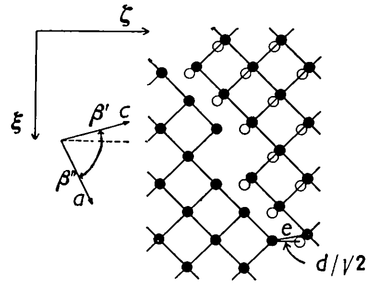

Fig. 2. The appearance of the border regions of the ReO_3-type blocks when the repulsion between metal atoms of MeO_6 octahedra sharing edges is taken into consideration (black metal atom circles). This arrangement corresponds to a displacement of all the metal atoms of the right block by $-(d/\sqrt{2})\delta$ (in the ξ-direction) and by $(d/\sqrt{2})\delta$ (in the ζ direction) from the atomic positions corresponding to regular MeO_6 octahedra (open circles). The oxygen atoms are omitted.

$$\delta = \sqrt{\{(e/d)^2-\tfrac{1}{4}\}}-\tfrac{1}{2}\,.$$

In order to simplify the mathematical expressions a few auxiliary variables were introduced. The finite width of the blocks, n, was thus formulated

$$n = (m+1)p+q\,,$$

where p and q are integers and the latter has values $0, 1, 2, 3, \ldots, m$ for unpuckered structures and $-1, 0, 1$ for puckered structures of the series Me_nO_{3n-1}. Furthermore, the monoclinic angle β was expressed by

$$\beta = \beta'+\beta''\,,$$

where β' and β'' represent the slopes of the c and a axes against the diagonal of the basic ReO_3-type mesh, as indicated in Fig. 2. The value of β'' is thus independent of n.

Table 1. *Geometrical characteristics of non-puckered structures* Me_nO_{3n-m+1} $(m \geq 2;\ n = p(m+1)+q,\ q = 0, 1, 2, \ldots, m)$

Symmetry: $P2/m$.
Unit-cell content: Me_nO_{3n-m+1}.
Unit-cell dimensions:

$$\begin{aligned}
a &= d\sqrt{(m^2+1)},\\
b &= d,\\
c &= (d/\sqrt{2})\sqrt{\{[n-(m-1)(p+1)+\delta]^2}\\
&\qquad\qquad +[(n+1)-(m+1)(p+1)-\delta]^2\};
\end{aligned}$$

$$\beta = \beta'+\beta'';\ \beta' = \operatorname{arctg}\left[\frac{(m+1)(p+1)-(n+1)+\delta}{n-(m-1)(p+1)+\delta}\right],\quad \beta'' = \operatorname{arctg}\left[\frac{m+1}{m-1}\right].$$

Metal atom positions $1(a)$, $1(e)$, or $2(n)$:

$$\begin{aligned}
x_i &= j\,\frac{d\sin(\beta'+45^\circ)}{2a\sin(180^\circ-\beta)}+\frac{k}{2},\\
y_i &= \tfrac{1}{2},\\
z_i &= j\,\frac{d\sin(\beta''-45^\circ)}{2c\sin(180^\circ-\beta)},
\end{aligned}$$

where

$$j = \begin{cases} 0, 2, 4, \ldots, (n-1) & \text{for } n \text{ odd}\\ 1, 3, 5, \ldots, (n-1) & \text{for } n \text{ even}\end{cases}$$

and

$$k = \begin{cases} 1 \text{ for } n < 2(m+1),\\ \qquad 3(m+1) \leq n < 4(m+1),\\ \qquad 5(m+1) \leq n < 6(m+1) \text{ etc.}\\[1ex] 0 \text{ for } 2(m+1) \leq n < 3(m+1),\\ \qquad 4(m+1) \leq n < 5(m+1) \text{ etc.}\end{cases}$$

Table 2. *Geometrical characteristics of puckered structures* Me_nO_{3n-1} $(m = 2;\ n = 3p+q,\ q = -1, 0, +1)$

Symmetry: $P2/a$.
Unit cell content: $2\,Me_nO_{3n-1}$.
Unit cell dimensions:

$$\begin{aligned}
a &= 2d\sqrt{5},\\
b &> d,\\
c &= (d/\sqrt{2})\sqrt{\{[2p-1+\delta]^2+[6p-2n-2-\delta]^2\}};
\end{aligned}$$

$$\beta = \beta'+\beta'';\ \beta' = \operatorname{arctg}\left[\frac{2n+2-6p+\delta}{2p-1+\delta}\right],\ \beta'' = \operatorname{arctg}\left[\frac{m+1}{m-1}\right].$$

Metal atom positions $2(e)$ or $4(g)$:

$$\begin{aligned}
x_i &= j\,\frac{d\sin(\beta'+45^\circ)}{2a\sin(180^\circ-\beta)}+\frac{k}{4},\\
y_i &= \tfrac{1}{2}+lv,\\
z_i &= j\,\frac{d\sin(\beta''-45^\circ)}{2c\sin(180^\circ-\beta)},
\end{aligned}$$

where

$$j = \begin{cases} 0, 2, 4, \ldots, (n-1) & \text{for } n \text{ odd}\\ 1, 3, 5, \ldots, (n-1) & \text{for } n \text{ even}\end{cases}$$

$$k = \begin{cases} 0 & \text{for } n \text{ even}\\ 1 & \text{for } n \text{ odd}\end{cases}$$

$$l = \begin{cases} +1 & \text{for } i = i_{\text{max.}}, i_{\text{max.}}-1, i_{\text{max.}}-3, i_{\text{max.}}-5, \ldots\\ -1 & \text{for } i = i_{\text{max.}}-2, i_{\text{max.}}-4, i_{\text{max.}}-6, \ldots\end{cases}$$

and v is a small positive quantity ($\sim 0{\cdot}1$).

The geometrical characteristics, also including the metal-atom positions, for unpuckered structures with $m \geq 2$ are summarized in Table 1 and the corresponding data for puckered structures of the series Me_nO_{3n-1} in Table 2. General expressions for the oxygen positions may of course also be derived. It was, however, not thought worth while to undertake this somewhat tedious work as the oxygen co-ordinates as obtained from experimental data must be relatively inaccurate and thus not very well fitted for comparisons with the ideal positions. Minor modifications (making δ equal to zero in the direction of the ξ axis of Fig. 2) will make the expressions of Table 1 also valid for lattices of the series Me_nO_{3n} ($m = 1$).

For reasons of lattice symmetry, other values of β and c have to be utilized for puckered structures Me_nO_{3n-1} $n \equiv 1$ (mod. 3) than those chosen for the corresponding unpuckered structures. This is also the background for the use of different sets of values for q in the expression $n = p(m+1)+q$ for unpuckered and puckered structures (*vide supra*).

An ideal V_2O_5*-type structure*

An interesting formal relation exists between structures of high values of m and that of vanadium pentoxide, which may be considered as built up of infinitely extending groups of MeO_6 octahedra joined by edges ($m = \infty$). For regular octahedra (cf. Fig. 3) this arrangement would correspond to an orthorhombic unit cell with the dimensions $a = 3d$, $b = c = d$ (d being the length of the space diagonal of the octahedron). The actual structure of vanadium pentoxide (Byström, Wilhelmi & Brotzen, 1950) shows a considerable deviation from this idealized structure, the VO_6 octahedra being highly distorted towards square VO_5 pyramids with an additional remote oxygen atom. The distortion is reflected by the axial ratio of the orthorhombic unit cell being $a:b:c = 3{\cdot}07:1{\cdot}17:0{\cdot}95$ (referred to a plausible value of $d = 3{\cdot}75$ Å). However, the vanadium pentoxide structure is able to dissolve considerable amounts of molybdenum trioxide, which modifies the structure towards a more regular octahedral arrangement (Magnéli, Oughton & Blomberg, 1951). The axial ratio for a solid solution with 14% of the vanadium(V)atoms substituted by molybdenum(VI)atoms (and the proper amount of vacant metal-atom sites) is $a:b:c = 3{\cdot}10:1{\cdot}14:0{\cdot}96$.

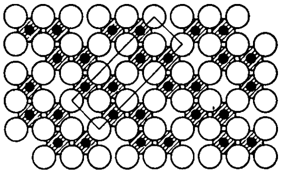
Fig. 3. The Me_2O_5 structure built up of regular MeO_6 octahedra. The unit mesh corresponds to the ac projection of an idealized V_2O_5-type structure, a being the longer axis.

X-ray patterns

A common feature of the X-ray diffraction patterns of the structures derived above will be the appearance of a sub-structure effect caused by the dominating influence of the ReO_3-type arrangement of the atoms. Large finite extension of the blocks, regularity of the

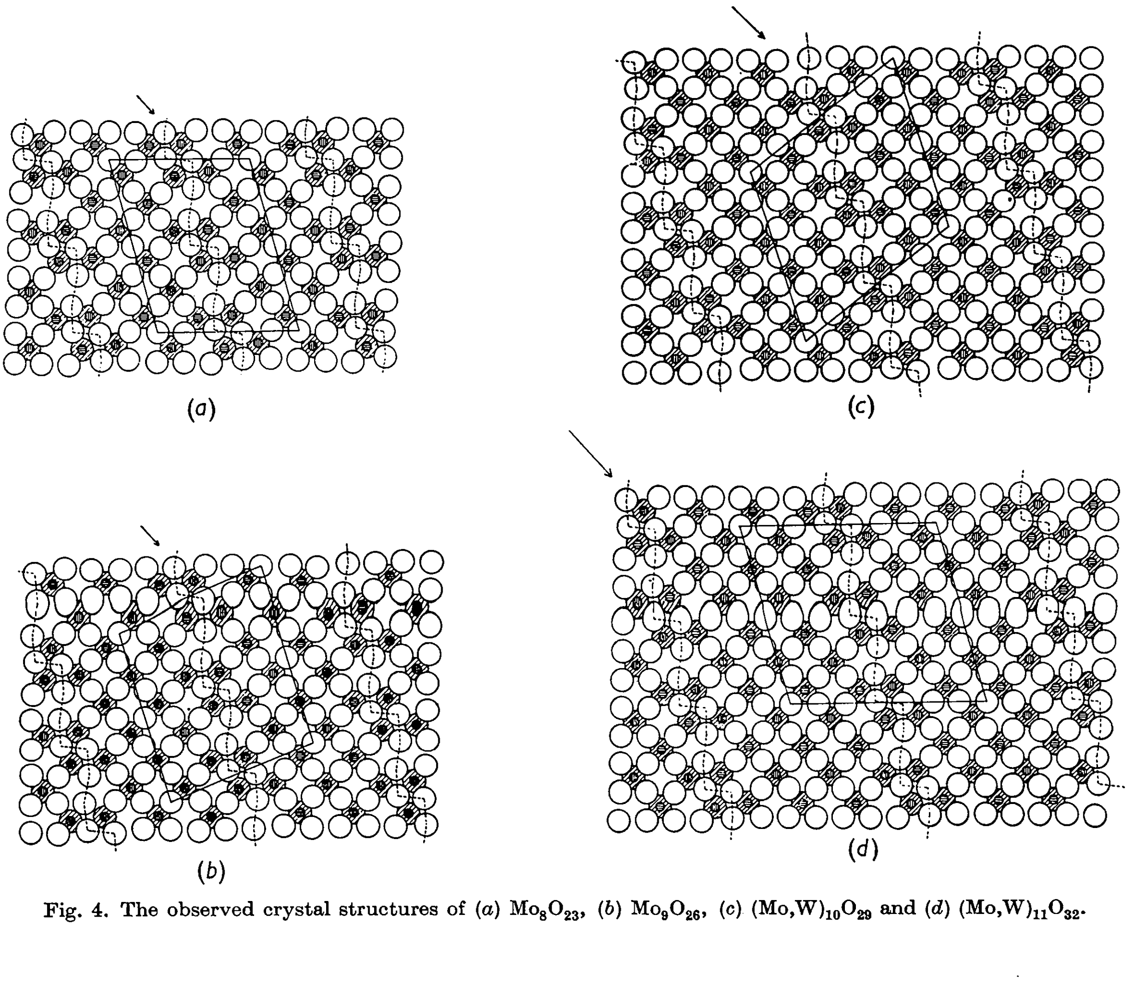
(a)
(b)
(c)
(d)

Fig. 4. The observed crystal structures of (a) Mo_8O_{23}, (b) Mo_9O_{26}, (c) $(Mo,W)_{10}O_{29}$ and (d) $(Mo,W)_{11}O_{32}$.

Table 3. *Comparison between observed and ideal unit-cell dimensions for oxides* Me_nO_{3n-1} *and* Me_nO_{3n-2}

		Observed unit cell dimensions				Ideal unit cell dimensions			
Oxide	m	a (Å)	b (Å)	c (Å)	β	a (Å)	b (Å)	c (Å)	β
Mo_8O_{23}	2	16·90	4·055	13·38	73° 73	16·77	> 3·75	13·81	73° 91
Mo_9O_{26}	2	16·74	4·019	14·53	95° 45	16·77	> 3·75	15·00	94° 58
$(Mo,W)_{10}O_{29}$	2	17·0	4·00	17·5	111°	16·77	> 3·75	17·76	110° 47
$(Mo,W)_{11}O_{32}$	2	16·6	4·00	18·7	74°	16·77	> 3·75	19·12	73° 23
$W_{20}O_{58}$	3	12·05	3·767	23·59	85° 28	11·86	3·75	23·37	84° 75

Table 4. *Comparison between observed and ideal atomic co-ordinates for oxides* Me_nO_{3n-1}

Space-group $P2/a$. (The co-ordinate values refer to sequences of atoms in the directions of the arrows of Fig. 4.)

			Observed co-ordinates			Ideal co-ordinates		
Oxide	Me atom	Point position	x	y	z	x	y	z
Mo_8O_{23}	Mo_1	4(g):	0·085	0·59	0·063	0·085	$> \frac{1}{2}$	0·063
	Mo_2	4(g):	0·254	0·41	0·188	0·257	$< \frac{1}{2}$	0·190
	Mo_3	4(g):	0·423	0·59	0·316	0·428	$> \frac{1}{2}$	0·316
	Mo_4	4(g):	0·596	0·59	0·445	0·599	$> \frac{1}{2}$	0·442
Mo_9O_{26}	Mo_1	2(e):	$\frac{1}{4}$	0·41	0	$\frac{1}{4}$	$< \frac{1}{2}$	0
	Mo_2	4(g):	0·456	0·59	0·113	0·458	$> \frac{1}{2}$	0·112
	Mo_3	4(g):	0·662	0·41	0·221	0·666	$< \frac{1}{2}$	0·224
	Mo_4	4(g):	0·869	0·59	0·334	0·874	$> \frac{1}{2}$	0·337
	Mo_5	4(g):	1·082	0·59	0·450	1·082	$> \frac{1}{2}$	0·449
$(Mo,W)_{10}O_{29}$	Me_1	4(g):	0·117	0·42	0·050	0·119	$< \frac{1}{2}$	0·050
	Me_2	4(g):	0·353	0·58	0·150	0·356	$> \frac{1}{2}$	0·151
	Me_3	4(g):	0·591	0·42	0·252	0·594	$< \frac{1}{2}$	0·252
	Me_4	4(g):	0·825	0·58	0·352	0·832	$> \frac{1}{2}$	0·352
	Me_5	4(g):	1·065	0·58	0·457	1·069	$> \frac{1}{2}$	0·453
$(Mo,W)_{11}O_{32}$	Me_1	2(e):	$\frac{1}{4}$	0·60	0	$\frac{1}{4}$	$> \frac{1}{2}$	0
	Me_2	4(g):	0·418	0·40	0·092	0·420	$< \frac{1}{2}$	0·092
	Me_3	4(g):	0·588	0·60	0·183	0·590	$> \frac{1}{2}$	0·183
	Me_4	4(g):	0·757	0·40	0·277	0·759	$< \frac{1}{2}$	0·275
	Me_5	4(g):	0·927	0·60	0·370	0·929	$> \frac{1}{2}$	0·366
	Me_6	4(g):	1·096	0·60	0·458	1·099	$> \frac{1}{2}$	0·458

MeO_6 octahedra and high scattering power of the metal atoms in comparison with that of oxygen will co-operate to give rise to single-crystal photographs with all strong reflexions concentrated in multiplets close to the reciprocal-lattice points of a primitive cubic sub-structure with the cell constant $a' = d$ (the space diagonal of the regular MeO_6 octahedron). In extreme cases all the interjacent reflexions may be too weak to be detectable in the X-ray patterns (Magnéli, 1951). If the metal-atom layers are puckered, the sub-structure will be tetragonal with $a' = d\sqrt{2}$ and c' slightly larger than d.

Comparison between observed and hypothetical structures

One of the essential interests in the considerations presented above is of course whether it is possible to prepare new chemical compounds with structures corresponding to these hypothetical atomic arrangements. Investigations of mixed molybdenum tungsten oxides recently carried out at this Institute have given an affirmative answer to this question. Thus, structure analyses of two such phases carried out on the basis of the geometrical discussions described above demonstrated the existence of the compounds $(Mo,W)_{10}O_{29}$ and $(Mo,W)_{11}O_{32}$, corresponding to members of the series Me_nO_{3n-1} with puckered metal-atom layers (Blomberg, Kihlborg & Magnéli, 1953). The crystal structures of the four homologues known at present are illustrated in Fig. 4. Further molybdenum tungsten oxide phases have been isolated and their X-ray patterns suggest that they are still higher members of this series. However, this matter has not so far been investigated in detail and merits further studies. Attempts to prepare compounds belonging to series other than Me_nO_{3n-1} are also desirable, $W_{20}O_{58}$ at present being the only known substance of this kind. It is obvious, however, that the identification of structures containing very wide blocks must be a rather intricate task, owing to the peculiar character of their X-ray patterns.

It is also of considerable interest to correlate the geometrical properties of the actually known structures with those of the hypothetical atomic arrangements. In this way it should be possible to get an idea of the feasibility of the arguments put forward in this article in predicting the properties of unknown sub-

Table 5. *Comparison between observed and ideal atomic co-ordinates for* $W_{20}O_{58}$

Space-group $P2/m$

W atom	Point position	Observed co-ordinates			Ideal co-ordinates		
		x	y	z	x	y	z
W_1	$2(n)$:	0·647	$\frac{1}{2}$	0·026	0·646	$\frac{1}{2}$	0·026
W_2	$2(n)$:	0·937	$\frac{1}{2}$	0·077	0·937	$\frac{1}{2}$	0·077
W_3	$2(n)$:	0·227	$\frac{1}{2}$	0·128	0·228	$\frac{1}{2}$	0·128
W_4	$2(n)$:	0·519	$\frac{1}{2}$	0·178	0·519	$\frac{1}{2}$	0·179
W_5	$2(n)$:	0·808	$\frac{1}{2}$	0·229	0·810	$\frac{1}{2}$	0·230
W_6	$2(n)$:	0·097	$\frac{1}{2}$	0·280	0·101	$\frac{1}{2}$	0·281
W_7	$2(n)$:	0·390	$\frac{1}{2}$	0·331	0·392	$\frac{1}{2}$	0·332
W_8	$2(n)$:	0·678	$\frac{1}{2}$	0·382	0·683	$\frac{1}{2}$	0·383
W_9	$2(n)$:	0·970	$\frac{1}{2}$	0·432	0·974	$\frac{1}{2}$	0·434
W_{10}	$2(n)$:	0·260	$\frac{1}{2}$	0·483	0·265	$\frac{1}{2}$	0·485

stances of this type which might exist. When calculating the data for the ideal structures a value of $d = 3{\cdot}75$ Å was chosen, which was supposed to be a reasonable value for the distance between the metal atoms of regular MeO_6 octahedra sharing corners. The distance between the metal atoms of octahedra joined by edges (e) was found to be 3·25–3·3 Å in Mo_8O_{23}, Mo_9O_{26} and $W_{20}O_{58}$, and this value, corresponding to $\delta = 0{\cdot}21$, was adopted here.

The observed and ideal unit-cell dimensions of the four known members of the series Me_nO_{3n-1}, and of $W_{20}O_{58}$, are listed in Table 3. The data for the simple oxides are obtained from powder photographs and those for the mixed oxides, the molybdenum:tungsten ratios of which are not accurately known, from single-crystal investigations. The deviations obtained for the monoclinic angles are throughout less than 1°. Comparisons of the lengths of the a and c axes will of course suffer from the inaccuracy of the value assigned to d. However, the deviations do not exceed 1·6% for the a axes. For the Me_nO_{3n-1} compounds, the observed c axes are throughout somewhat shorter (less than 3·1%) than the ideal ones. The observed a and c axes for $W_{20}O_{58}$ are both a little longer than the ideal values. Introducing a d value equal to the observed length of the b axis of this substance (3·767 Å instead of 3·75 Å) will reduce this small deviation by giving ideal dimensions of 11·91 Å and 23·48 Å respectively.

A comparison between the structural details of the observed and ideal structures may be made from the metal-atom positions given in Table 4 (for Me_nO_{3n-1}) and Table 5 (for $W_{20}O_{58}$). As the inaccuracy of the experimentally derived x and z co-ordinates is likely to amount to a few per mille of the axial lengths, the agreement must be considered to be almost perfect for all the compounds.

The close agreement thus found to exist between the observed and hypothetical structures evidently fully justifies the assumptions concerning the atomic arrangement within the blocks and at their joint planes made when deriving the geometrical properties of the latter. The expressions given in Table 1 and 2 are also likely to be capable of predicting the detailed structural arrangement of at present unknown members of these series. They have already proved to be of value when deriving the crystal structures of $(Mo,W)_{10}O_{29}$ and $(Mo,W)_{11}O_{32}$.

This work has been carried out in connection with investigations on oxides and oxide systems financially supported by the Swedish Natural Science Research Council.

References

Blomberg, B., Kihlborg, L. & Magnéli, A. (1953). *Ark. Kemi*, **6**. In the press.

Byström, A., Wilhelmi, K.-A. & Brotzen, O. (1950). *Acta chem. scand.* **4**, 1119.

Magnéli, A. (1948). *Acta chem. scand.* **2**, 501.

Magnéli, A. (1950*a*). *Ark. Kemi*, **1**, 513.

Magnéli, A. (1950*b*). *Nova Acta Reg. Soc. Sci. Upsal.* (4), **14**, No. 8.

Magnéli, A. (1951). *Acta Cryst.* **4**, 447.

Magnéli, A. (1952). *Research*, **5**, 394.

Magnéli, A., Oughton, B. M. & Blomberg, B. (1951). *Acta chem. scand.* **5**, 581, 585.

Strukturbericht. 1928–1932, (1937). p. 32.