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The Crystal Structure of $Mo_{17}O_{47}$

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A crystal structure determination has been carried out on the $\varkappa$-molybdenum oxide, which has confirmed the proposed formula $Mo_{17}O_{47}$ and the orthorhombic space-group *Pba*2 for this phase.

The structure may be considered as built up from MoO_6 octahedra and pentagonal MoO_7 bipyramids. The Mo—O distances within the latter are rather unequal suggesting that the coordination is not so high as sevenfold. Fairly short O—O distances (mean value 2.32 Å) have been observed within the pentagonal rings of the oxygens in these bipyramids.

The polyhedra are connected in one dimension through common corners and in two dimensions by sharing corners and edges. A distance of 2.64 Å between two molybdenum atoms suggests a direct bond between them of the same kind as is known for example in several transition metal dioxides.

The structure is closely related to that of $W_{18}O_{49}$, previously determined by Magnéli, and this relationship is discussed.

The results of a phase analysis study of the MoO_2—MoO_3 region of the molybdenum — oxygen system were recently published in this journal [1]. In the course of these investigations a phase of composition near $MoO_{2.78}$ was observed formed below 560° ± 10°C and was designated the *$\varkappa$-oxide*. From its X-ray powder pattern, obtained with a Guinier focussing camera using Cu*Kα* radiation, the following dimensions were derived for the orthorhombic unit cell:

$$a = 21.61_5\ \text{Å}, \qquad b = 19.63_2\ \text{Å}, \qquad c = 3.951_5\ \text{Å}.$$

The observed density was found to be consistent with the formula $Mo_{17}O_{47}$, having 2 formula units in the unit cell.

A structure determination of this phase has now been carried out on the basis of single crystal data and is presented in this article.

EXPERIMENTAL

Details concerning the preparation of the oxide are given in Ref.[1] The single crystals obtainable were in the form of very thin, fragile needles which were too small to give reflexions with Mo*K* radiation within reasonable time. The crystal investigated had a length of 0.15 mm and a rectangular cross-section of 0.012 × 0.002 mm^2. The pronounced needle shape allowed the crystal to be rotated about the needle axis only, this being the *c*-axis of the unit cell. The layer lines *hk*0 to *hk*3 were registered in a Weissenberg camera with Cu*Ka* radiation using the multiple film technique. The intensities were estimated visually and the various layer lines were correlated by exposing parts of each of them on the same pack of films, using carefully controlled exposure times and radiation conditions [2].

A few photographs were also taken with a Buerger precession camera, which allowed 00*l* reflexions to be registered.

Lorentz-polarization corrections were applied by the method given by Löfgren [3]. The *hk*0 reflexions were corrected for the effect of absorption by means of a graphical method developed by Hesse [4]. In this way a set of relative structure amplitudes were obtained which were later brought to an absolute scale by comparison with the calculated structure factors.

Most of the calculations were carried out by means of the digital computers BESK and Facit EDB in Stockholm. A description of some of the programmes used with these machines has recently been published [5,6]. The atomic scattering curves of Thomas and Umeda [7] (for Mo) and Berghuis *et al.*[8] (for O) were used in the form of analytical representations given by Appel [9].

DETERMINATION OF THE STRUCTURE

The reflexions *h*0*l* and 0*kl* are absent for odd *h* and *k* which suggests the space groups *Pba*2 (No. 32) or *Pbam* (No. 55). In *Pbam* there are mirror planes perpendicular to the *c* axis and owing to the shortness of this axis it is unlikely that an atom could be in a general position relative to these symmetry elements. If the atoms were situated on the mirror planes, *i.e.* on one or both of the planes $z = 0$ and $z = \frac{1}{2}$, the observed relative intensities of the 00*l* reflexions could not be explained. It was therefore assumed that the space group is *Pba*2, which has been confirmed by the structure determination.

The projection on (001) is centro-symmetrical in contrast to the space group as a whole, and in the present case is the most important one as it contains the two long axes. The atomic *x* and *y* coordinates were derived exclusively from this projection on the basis of *hk*0 data, and when they had been established the *z* parameters were determined with use of full *hkl* data.

a. Determination of the *x* and *y* coordinates

In the space group *Pba*2 there are 2- and 4-fold positions. As the unit cell was supposed to contain 34 Mo atoms, two of these must be in one of the two 2-fold positions. Starting from this, it was possible to find an arrangement of the metal atoms that fully accounted for the Patterson projection $P(UV)$ shown in Fig. 1a. After two cycles of computation of structure factors $F_c(hk0)$ and electron density projections $\varrho(XY)$, correct signs could be assigned to all the observed structure amplitudes $|F(hk0)|$.

The electron density maps showed minor maxima, which could reasonably be interpreted as being due to 4 × 15 oxygen atoms (O_{10}—O_{24}, *cf.* Fig. 2). In a difference synthesis, where the contribution from all the Mo atoms had been subtracted, the remaining $2 \times 1 + 4 \times 8$ oxygen atoms (O_1—O_9) were clearly revealed as rest maxima close to the positions of the Mo atoms. These maxima were about 20 % lower than the other oxygen peaks, even after the

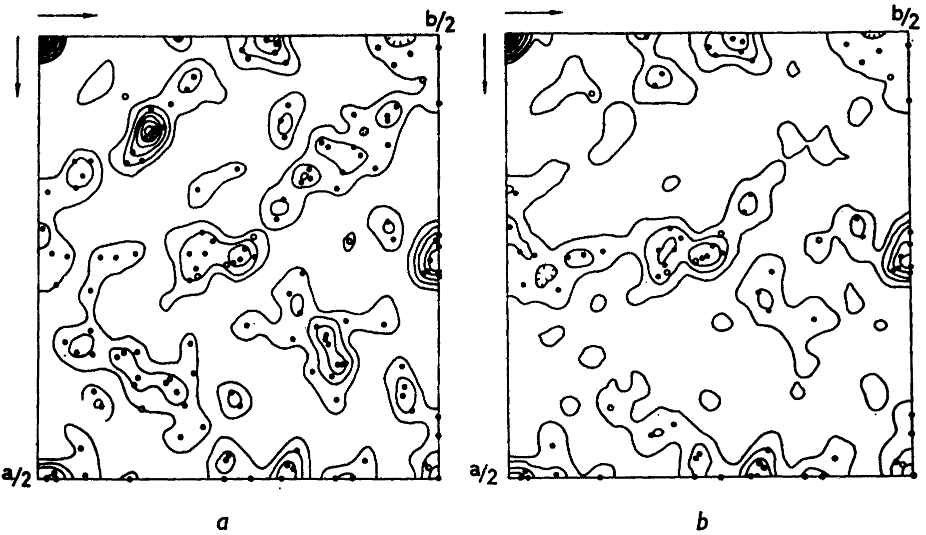

Fig. 1. Patterson function and corresponding Mo—Mo vector set obtained from the final atomic coordinates. Full circles indicate vectors of multiplicity 2, open circles multiplicity 1.
a. Projection on (001), $P(UV)$. *b.* Section at $w = 0$, $P(UV0)$.

refinement. Their heights are, however, very sensitive to the scattering factor used for molybdenum, and the fact that the calculated structure factors were based on the scattering curve of zero-valent molybdenum, can therefore explain the difference.

Structure factors were calculated with the coordinates of the strong peaks in $\varrho_o(XY)$ given to both Mo_1—Mo_9 and O_1—O_9 and the coordinates of the remaining oxygens obtained from the difference map. The corresponding $\varrho_c(XY)$ function was calculated and the back-shifts of the strong peaks were applied on the Mo positions. New parameters for all the oxygen atoms were obtained from a difference map, and these were used in a second back-shift of the Mo-coordinates. These last shifts did not exceed 0.007 Å. The final oxygen parameters were then derived from a new difference map.

An isotropic, over-all temperature factor with the value $B = 0.81$ Å^2 was used in the calculations. The reliability index obtained after this refinement is given in Table 1.

The x and y coordinates thus obtained are given in Table 2, together with standard deviations calculated according to Cruickshank [10]. For the oxygens O_1—O_9 no standard deviations are given, as the parameters derived for them may be systematically influenced by the presence of the Mo atoms. The coordinates of these latter atoms on the other hand are not likely to be seriously in error owing to the overlapping oxygen atoms.

Table 1. The reliability indices R of various layer lines. $R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$ calculated from observed reflexions only.

Layer line	Number of independent reflexions	R
$hk0$	259	0.073
$hk1$	219	0.100
$hk2$	201	0.109
$hk3$	90	0.108

b. Determination of the z coordinates

From the appearance of some regions of the three-dimensional Patterson function, the conclusion could be drawn, that all the Mo atoms are situated near to two planes perpendicular to the c axis with a separation of $\Delta z \approx 0.16$. It was possible to distribute these atoms on two planes in such a way that the Patterson section $P(UV0)$ shown in Fig. 1b could be fully explained. The calculated phase angles were assigned to the observed structure factor amplitudes, and electron density sections were computed, from which the coordinates of $O_{10}-O_{24}$, as well as new parameters for Mo_1-Mo_9 were obtained. Maxima corresponding to the oxygens O_1-O_9 were observed around $z = 0$, but they were very broad and less well-shaped due to partly coinciding with the termination of series effects from the heavy atoms. In the calculations they were assigned the parameter values $z(O_n) = z(Mo_n) + \frac{1}{2}$, where $z(Mo_n)$ is the coordinate of the molybdenum atom with approximately the same x and y parameters.

After two more phase angle — electron density cycles a back-shift was performed, which yielded shifts within $\Delta z \leq 0.003$ for Mo and $\Delta z \leq 0.021$ for $O_{10}-O_{24}$. The coordinates thus obtained are listed in Table 2. The final z parameters of O_1-O_9 given in Table 2 have been obtained by consideration of interatomic distances. If these atoms were situated exactly halfway between the two molybdenum neighbours in the c-axis direction, they would in most cases have four oxygen atoms very close on one side and four others rather distant on the other side. The z coordinates have therefore been choosen so as to make the distances $O_{1-9}-O_{10-24}$ greater than 2.52 Å and approximately equal on both sides. This can be attained if Mo—O distances as short as 1.69 Å are allowed.

The reliability indices are given in Table 1.

The standard deviations calculated according to Cruickshank [10] (multiplied by 2 on behalf of the non-centrosymmetry) are $\sigma_{Mo}(z) = \pm 0.03$ ($= \pm$ 0.12 Å) and $\sigma_O(z) = \pm 0.16$ ($= \pm$ 0.64 Å). The low number of terms in the Fourier synthesis along the z axis and the fact that no absorption correction was applied to the reflexions hkl, $l \neq 0$, contributes to the large $\sigma(z)$ value. As the absorption coefficient is fairly constant for reflexions with the same values of h and k, this effect can not give rise to serious errors in the z parameters. For space reasons the value of $\sigma_O(z)$ seems much too high to have any real meaning. A deviation $\Delta z = 0.6$ Å for an oxygen atom decreases the distances to some

Table 2. The crystal structure of $Mo_{17}O_{47}$

Space-group: *Pba*2 (No. 32)
Unit cell dimensions: $a = 21.61_5$ Å
$b = 19.63_2$ Å
$c = 3.951$ Å

Cell content: 2 $Mo_{17}O_{47}$
2 Mo and 2 O in 2 × 2(*a*): $(0,0,z;\ \frac{1}{2},\frac{1}{2},z)$
32 Mo and 92 O in 31 × 4(*c*): $(x,y,z;\ \bar{x},\bar{y},z;\ \frac{1}{2}-x,\ \frac{1}{2}+y,z;\ \frac{1}{2}+x,\ \frac{1}{2}-y,z)$

Atom	Position	$x \pm \sigma(x)$	$y \pm \sigma(y)$	$z \pm \sigma(z)$
Mo_1	2 (*a*)	0	0	.579 ± .030
Mo_2	4 (*c*)	.0244 ± .0002	.2606 ± .0002	.581 ± .030
Mo_3	4 (*c*)	.1299 ± .0002	.1189 ± .0002	.425 ± .030
Mo_4	4 (*c*)	.1355 ± .0002	.4005 ± .0002	.434 ± .030
Mo_5	4 (*c*)	.2424 ± .0002	.2573 ± .0002	.575 ± .030
Mo_6	4 (*c*)	.2881 ± .0002	.0653 ± .0002	.579 ± .030
Mo_7	4 (*c*)	.3824 ± .0002	.1944 ± .0002	.428 ± .030
Mo_8	4 (*c*)	.3851 ± .0002	.3661 ± .0002	.424 ± .030
Mo_9	4 (*c*)	.4657 ± .0002	.0556 ± .0002	.565 ± .030
O_1	2 (*a*)	0	0	.01
O_2	4 (*c*)	.020	.266	.01
O_3	4 (*c*)	.126	.115	.98
O_4	4 (*c*)	.140	.396	.98
O_5	4 (*c*)	.246	.251	.00
O_6	4 (*c*)	.288	.069	.01
O_7	4 (*c*)	.383	.191	.00
O_8	4 (*c*)	.392	.360	.00
O_9	4 (*c*)	.465	.052	.05
O_{10}	4 (*c*)	.076 ± .002	.045 ± .002	.46
O_{11}	4 (*c*)	.060 ± .002	.181 ± .002	.52
O_{12}	4 (*c*)	.093 ± .002	.324 ± .003	.44
O_{13}	4 (*c*)	.059 ± .002	.462 ± .005	.57
O_{14}	4 (*c*)	.206 ± .002	.067 ± .002	.48
O_{15}	4 (*c*)	.180 ± .002	.195 ± .004	.46
O_{16}	4 (*c*)	.203 ± .002	.335 ± .002	.50
O_{17}	4 (*c*)	.191 ± .002	.475 ± .002	.54
O_{18}	4 (*c*)	.297 ± .002	.165 ± .003	.48
O_{19}	4 (*c*)	.330 ± .002	.280 ± .003	.48
O_{20}	4 (*c*)	.325 ± .002	.427 ± .004	.41
O_{21}	4 (*c*)	.380 ± .002	.091 ± .002	.56
O_{22}	4 (*c*)	.465 ± .002	.160 ± .003	.50
O_{23}	4 (*c*)	.434 ± .002	.275 ± .006	.52
O_{24}	4 (*c*)	.455 ± .002	.411 ± .002	.52

of its oxygen neighbours to generally below 2.30 Å. In Table 3, where interatomic distances *d* are listed, the standard deviations are given only for those distances where $\sigma(z)$ makes only a small contribution to $\sigma(d)$, and the more probable value $\sigma_0(z) = \pm 0.3$ Å was used in these cases.

Copies of a table of observed and calculated $|F(hkl)|$ values may be obtained on request.

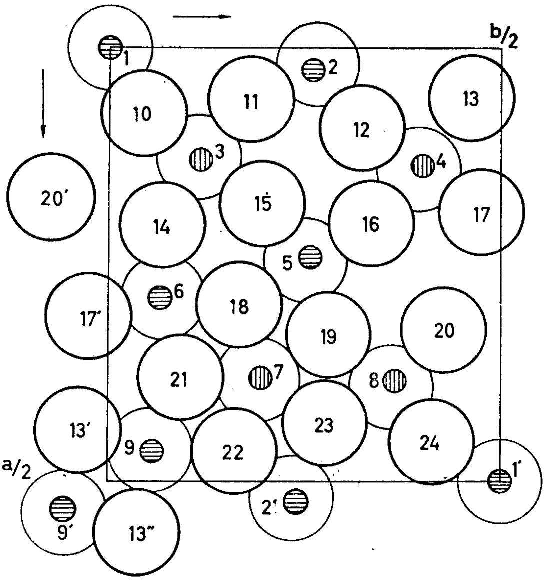

Fig. 2. Numbering of the atoms. Small circles = molybdenum. Large circles = oxygen. The numbers 1 to 9 refer to both molybdenum and oxygen.

DESCRIPTION OF THE STRUCTURE

The structural elements can, with one exception, be considered as distorted MoO_6 octahedra, coupled together by sharing corners or edges. The exception is the coordination polyhedron around Mo_7, which is fairly close to a pentagonal bipyramid.

Along the c axis, the extension of the polyhedra is one identity period. The coupling between them in this direction is brought about exclusively through common corners formed by the atoms O_1-O_9, which all lie at about the same height $z \approx 0$. The metal atoms are distorted from the centre of the polyhedra by an amount $\Delta z \approx \pm 0.08$, the distortion being in the same direction for Mo atoms with about the same x coordinates. The metal atoms thus form corrugated layers, as in Fig. 3.

Perpendicular to the c axis the polyhedra are linked together in a rather complicated way, which is best illustrated by Fig. 3. Only one fifth of the octahedra are of ReO_3 type, *i.e.* share all six corners with six neighbouring octahedra.

Mo_7 is the centre of an interesting arrangement, which has been found in $W_{18}O_{49}$ [11] (see below under Discussion) but has no counterpart among the other molybdenum oxides whose crystal structures are known at present. It has five Mo neighbours at the corners of a (puckered) pentagon, the projection of which along [001] is fairly regular. The distances to these corner atoms are 3.25—3.37 Å, which is normal for MoO_6 octahedra sharing edges [12]. The

Table 3. Interatomic distances d in Å.

Mo—Mo	d	$\pm\sigma(d)$
1 3	3.70	0.03
2 3	3.65	0.03
2 4	3.69	0.03
3 5	3.69	0.03
3 6	3.63	0.03
4 5	3.68	0.03
5 6	3.90	0.006
5 7	3.32	0.03
5 8	3.80	0.03
6 7	3.31	0.03
6 9	3.84	0.006
6 4′	3.68	0.03
7 8	3.37	0.006
7 9	3.31	0.03
7 2′	3.25	0.03
8 1′	3.67	0.03
8 2′	3.95	0.03
9 4′	3.78	0.03
9 9′	2.639	0.007
9 2′	3.83	0.006
9′ 4′	3.81	0.03
n *n*′ along [001]	3.951	

Mo—O	d	$\pm\sigma(d)$
1 1	1.70	
1 1′	2.25	
1 10	1.92	0.08
1 24′	2.00	0.10
2 2	1.70	
2 2′	2.26	
2 11	1.76	0.08
2 12	2.02	0.12
2 22′	2.04	0.08
2 23′	2.10	0.08
3 3	2.19	
3 3′	1.76	
3 10	1.87	0.06
3 11	1.97	0.10
3 14	1.94	0.08
3 15	1.85	0.06
4 4	2.14	
4 4′	1.81	
4 12	1.77	0.06
4 13	2.12	0.12
4 16	1.97	0.08
4 17	1.94	0.08
5 5	1.70	
5 5′	2.25	
5 15	1.87	0.10
5 16	1.77	0.08
5 18	2.20	0.10
5 19	1.98	0.10
6 6	1.72	
6 6′	2.23	
6 14	1.83	0.10
6 17′	1.83	0.06
6 18	2.00	0.10
6 21	2.06	0.06
7 7	2.25	
7 7′	1.70	
7 18	1.94	0.08
7 19	2.04	0.08
7 21	2.10	0.10
7 22	1.93	0.08
7 23	1.96	0.10
8 8	1.69	
8 8′	2.28	
8 19	2.08	0.08
8 20	1.76	0.08
8 23	2.10	0.08
8 24	1.80	0.08
9 9	2.05	
9 9′	1.90	
9 13′	1.91	0.06
9 13″	2.04	0.06
9 21	1.97	0.06
9 22	2.07	0.08

O—O	d	$\pm\sigma(d)$
12 16	2.40	0.07
18 19	2.37	0.07
18 21	2.33	0.07
19 23	2.24	0.07
21 22	2.30	0.07
22 23	2.36	0.07
all other	$\geq$ 2.53	

distances from Mo_7 to the five oxygen neighbours O_{18}, O_{19}, O_{21}, O_{22}, and O_{23} range from 1.93 to 2.10 Å, with a mean value of 1.99 Å, which is somewhat greater than the mean 1.94 Å for the rest of the Mo_{1-9}—O_{10-24} distances. As the distances to the two remaining oxygens, O_7 and $O_{7'}$, are very unequal,

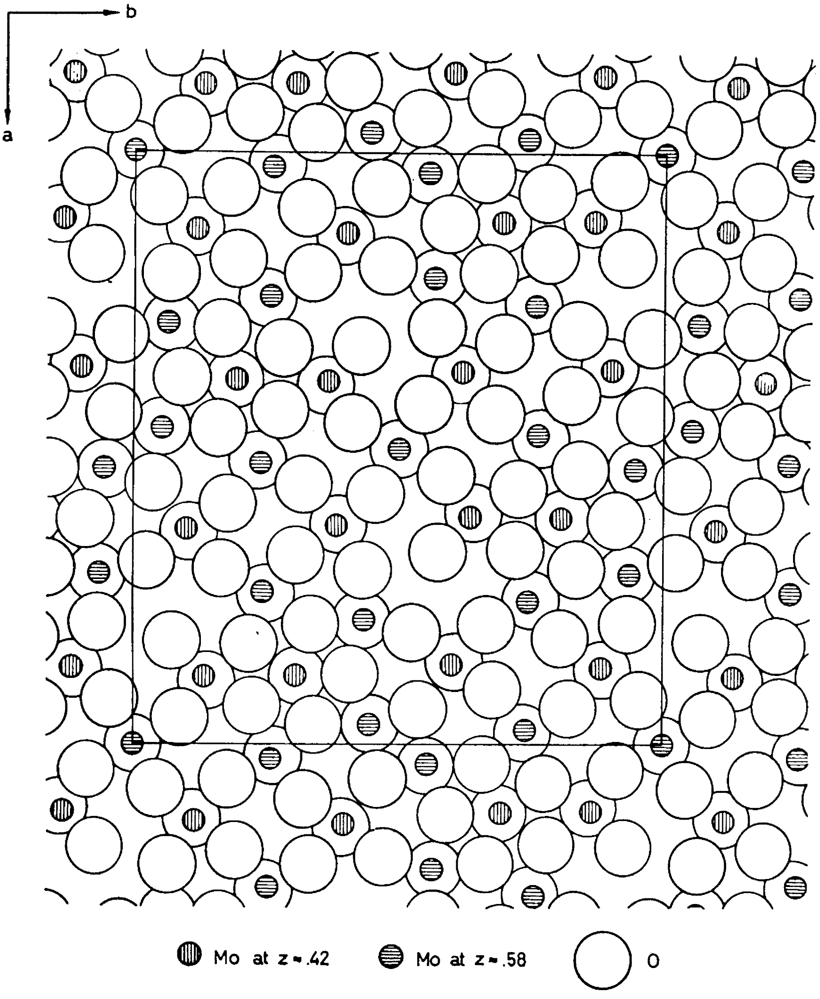

Fig. 3. The structure $Mo_{17}O_{47}$ viewed along [001]. The extension of one unit cell indicated. The oxygen atom above each molybdenum, in a position identical with that below it, has not been shown.

viz. 2.2 and 1.7 Å, the coordination can not be regarded as strictly sevenfold. The oxygens within the pentagon are very close together, the mean O—O distance being 2.32 Å, which is considerably shorter than has been observed for other molybdenum oxides.

The distance between Mo_9 and $Mo_{9'}$, which are related by a 2-fold axis, is only 2.639 Å. This indicates a bond between these atoms of the same kind that has been observed for example in MoO_2[13] and several other dioxides and dioxide systems [14] and recently also in low-Ti_3O_5[15]. In $W_{18}O_{49}$ the correspond-

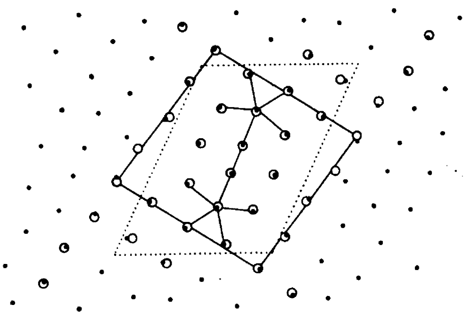

Fig. 4. Comparison between the metal atom patterns of $W_{18}O_{49}$ and $Mo_{17}O_{47}$; projection along the short axes. Dots = W positions in $W_{18}O_{49}$; dotted lines = extension of the unit cell of $W_{18}O_{49}$; circles = corresponding Mo positions in $Mo_{17}O_{47}$. The arrangement in two pentagons is indicated and the rhombic unit building up the structure of $Mo_{17}O_{47}$ also shown.

ing distance is 2.60 Å [11]. A formal treatment, where each oxygen atom is assigned 2 valence electrons taken equally from its molybdenum neighbours [15], yields a number of $2\frac{2}{3}$ valence electrons available for the formation of this bond, which fits well into the diagram of metal-metal bond lengths *versus* available valence electrons given by Marinder and Magnéli [14].

The atom O_{20} is bonded to only one molybdenum *viz.* Mo_8. The distance between them is 1.76 Å, which is among the shortest of the Mo—O distances in this plane. Such singly bonded oxygens exist in MoO_3, where the corresponding bond length is 1.8 Å [16], but has not been found in any other molybdenum or tungsten oxide.

DISCUSSION

The molybdenum oxides, besides $Mo_{17}O_{47}$, whose crystal structures are known at present are: MoO_3 with a layer structure [16-18], Mo_9O_{26} (mon.)[2], Mo_8O_{23} [2] and Mo_4O_{11} (o.-rh.) [19] containing two-dimensionally infinite blocks of the ReO_3 type, MoO_2 of deformed rutile type [13], and the metallic oxide Mo_3O, probably of defective BiF_3 type [20]. Although MoO_6 octahedra can be distinguished as the main structural element in all but the last of these structures, these do not show any strong resemblance to the present structure. In the closely interrelated phases Mo_9O_{26} (mon.) and Mo_8O_{23} the metal atoms form layers which are puckered to about the same degree as in $Mo_{17}O_{47}$, but the arrangement within these layers is quite different.

There is, however, an extremely interesting and close relationship between the present structure and that of γ-tungsten oxide, $W_{18}O_{49}$, determined by Magnéli [11]. This structure is monoclinic with the space group $P2/m$. In Fig. 4 the black dots indicate the positions of the W atoms in a projection along the unique axis, and the extension of one unit cell is marked by dotted lines (the origin has been moved to ($\frac{1}{2}$, 0, $\frac{1}{2}$) compared with Magnéli's notation). If the 2-fold axis in the centre of this cell is brought into coincidence with the 2-fold axis at (0, $\frac{1}{2}$, z) or ($\frac{1}{2}$, 0, z) in $Mo_{17}O_{47}$, there is an almost complete accordance

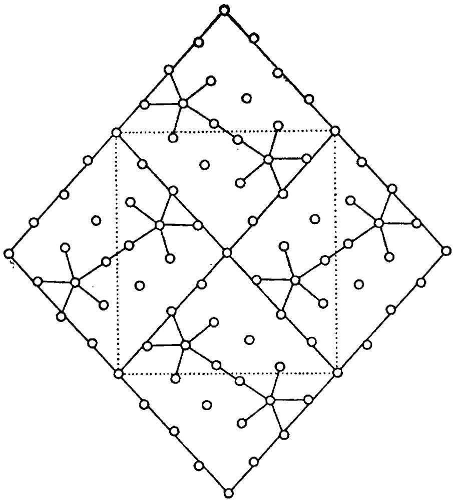

Fig. 5. The manner in which the $Mo_{17}O_{47}$ structure is built up from the rhombic unit of Fig. 4. Only metal atoms are indicated. Dotted lines show the extension of the unit cell.

between the metal atom patterns within an area containing 38 metal atoms. This can be seen in Fig. 4 where the positions of the Mo atoms within this area are marked by small circles. The pattern within the rhomb indicated by full lines builds up the $Mo_{17}O_{47}$ structure in the way shown in Fig. 5.

The oxygen positions in $W_{18}O_{49}$ were not revealed experimentally because of the unfavorable ratio between the scattering factors of oxygen and tungsten, but were derived by Magnéli from spatial considerations. Nevertheless they agree with those of $Mo_{17}O_{47}$ to about the same extent as do the metal positions. Oxygen-oxygen distances as short as 2.32 Å were quite naturally avoided, and this gave rise to a less symmetrical arrangement of oxygens around the tungsten atom equivalent to Mo_7, *i.e.* within the pentagons. It now seems most probable, however, that the arrangement is the same in $W_{18}O_{49}$ as in $Mo_{17}O_{47}$ in this respect too.

Both structures are thus built up from blocks, containing the two centered pentagons of metal atoms joined by a short metal-metal bond, and the essential difference between them is the way in which these blocks are mutually connected.

The wide, empty channels in $W_{18}O_{49}$, bordered by rings of six octahedra and running through the structure along the unique axis, have no counterpart in $Mo_{17}O_{47}$. Also in this structure, six octahedra are connected so as to form a ring, but in one of these octahedra the coupling is across a diagonal, leaving an oxygen atom (O_{20}) in the middle of the ring which fills up most of the available space. In spite of this, the oxygen packing is equally dense on the average in both structures, since the unit cell volume divided by the number of oxygen atoms has the same value 17.8 Å^3.

There is a further difference that becomes clear when the conditions in the third direction are examined. In $Mo_{17}O_{47}$ the metal atoms form layers which are puckered with an amplitude of ± 0.3 Å, while in $W_{18}O_{49}$ all tungsten atoms are situated at the same height (on a mirror plane). This is partly reflected in the length of the corresponding axis, which is 3.951 Å in $Mo_{17}O_{47}$ and 3.775 Å in $W_{18}O_{49}$ [21]. The same difference between molybdenum and tungsten has been found in the closely interrelated structures of Mo_8O_{23} [2], Mo_9O_{26} (mon.)[2] and $W_{20}O_{58}$ [22], and has been discussed by Magnéli [23]. An analogous puckering of the layers in the $W_{18}O_{49}$ structure would imply doubling of the unit cell.

Although it can not be excluded that a molybdenum oxide of the $W_{18}O_{49}$ type or a tungsten oxide of the $Mo_{17}O_{47}$type may form at conditions different from those hitherto used in the phase analysis of the Mo—O [1] and W—O [24] systems, there is no evidence for their existence at present. A study of the extent to which molybdenum and tungsten can replace each other in $Mo_{17}O_{47}$ and $W_{18}O_{49}$ would perhaps throw light on these problems.

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