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The Crystal Structure of Mo_4O_{11} (γ-Molybdenum Oxide)

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In a paper from this Institute [1] on X-ray studies of the products obtained by heating mixtures of molybdenum and molybdenum trioxide *in vacuo* a phase (γ-molybdenum oxide) was described which formed at about 650—700° C from preparations of compositions between $MoO_{2.85}$ and $MoO_{2.72}$. Mo_4O_{11} was given as a probable formula of this oxide. In a recent notice Glemser and Lutz [2] report a molybdenum oxide (β-phase according to their notation) evidently identical with the phase mentioned above. Their statement of a homogeneity range from $MoO_{2.75}$ to $MoO_{2.65}$, derived from X-ray data and measurements of electrical resistance, disagrees with our observation that no displacements of the powder photograph reflections, indicating an extended homogeneity range, could be detected.

Crystals of γ-molybdenum oxide suitable for single-crystal investigations with X-rays have now been obtained by prolonged heating of the oxide. They form small reddish-violet thin tablets of orthorhombic symmetry. The crystal actually used for this purpose was picked out from a preparation $MoO_{2.80}$ heated at about 700° C for 45 days. From Laue photographs the Laue symmetry was found to be D_{2h}—$m\,m\,m$. Rotation and Weissenberg photographs were taken around the axes [0 1 0] (layer lines 0—6) and [0 0 1] (the equator layer line) with Mo-K radiation. Correlation between the intensity scales of the former photographs was brought about by means of the reflections $h\,k\,0$ of the latter. The intensities were estimated visually, 4 : 2 : 1 being adopted as the intensity ratio of Mo-$K\alpha_1$, Mo-$K\alpha_2$, and Mo-$K\beta$ radiation. Relative values of F^2_{hkl} were obtained by multiplying the intensity values with the factor $\cos^2\mu \cdot \sin \Upsilon \; (1 + \cos^2 2\Theta)$ utilizing the curves given by Chia-Si Lu [3]. The temperature factor was neglected.

The dimensions of the orthorhombic unit cell as calculated from the single crystal photographs are:

$$a = 24.4 \text{ Å}, \; b = 5.45 \text{ Å}, \; c = 6.70 \text{ Å}, \; V = 890 \text{ Å}^3.$$

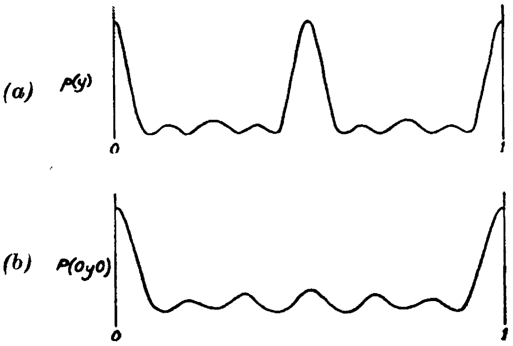

Fig. 1. a. *Projection of the Patterson function on the b axis, p(y).*
b. *The Patterson function along the b axis, P(0 y 0).*

For a preparation $MoO_{2.75}$, heated at 700° C for 100 hours, a density of 4.18 was measured. This corresponds to 16.0 $MoO_{2.75}$ units (4 Mo_4O_{11}) per cell.

Reflections $h\ k\ 0$ only appear when h is even and reflections $0\ k\ l$ only when $k + l$ is even. This is characteristic of the space-groups D_{2h}^{16}-*Pnma* and C_{2v}^{9}-$Pn2_1a$. The fact that the number of points corresponding to the point positions of these space-groups are all four or multiples of four gives support to the above assumption concerning the cell content.

MOLYBDENUM POSITIONS

The projection of the Patterson function * on the *b* axis, p(y), Fig. 1 a, only showing strong maxima at $y = 0$ and $\frac{1}{2}$, indicates that all the heavy metal atoms are arranged in or close to two planes normal to [0 1 0] and at a distance of $b/2$. However, the only strong maximum of the Patterson function along the *b* axis, P(0 y 0), Fig. 1 b, is the peak at the origin, which excludes the presence of metal atoms related by mirror planes. If *Pnma* is the actual space-group the Mo atoms thus must be situated in the mirror planes and occupy fourfold positions 4(c) of that space-group. The conception of the Mo atoms being arranged in this way is supported by the appearance of the

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* As far as possible all Fourier summations were carried out by means of the rapidly working Hägg-Laurent machine [4]. However, in the actual performance the machine only permits a maximum wave number of 16 and determination of the sum at intervals of 6° (and of course at intervals of 3° for even wave numbers up to 32), while h indices up to 34 were observed in the photographs. The calculations were then performed either by means of the Robertson strips [5] (maximum wave number 22) or without special calculating means. In the x direction the final summations were carried out at intervals of 3°.

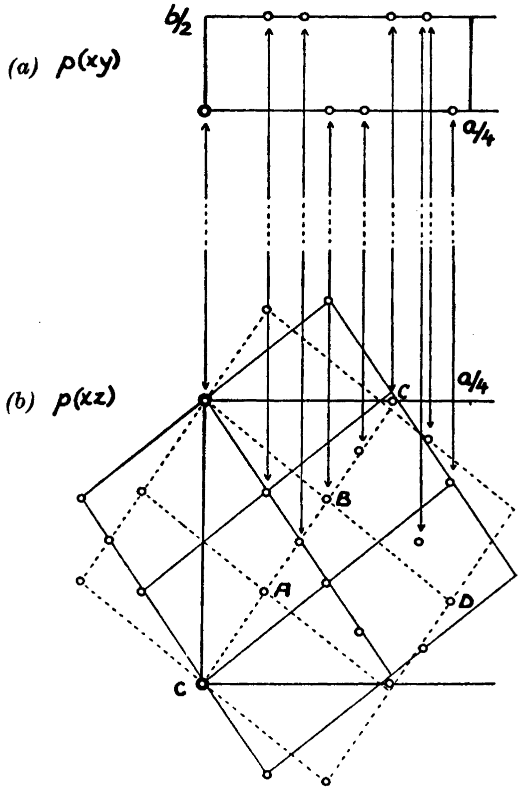

Fig. 2. a. Projection of the Patterson function parallel to [0 0 1], p(xy). b. Projection of the Patterson function parallel to [0 1 0], p(xz). Only the heavy maxima within the region $0 < x < \frac{a}{4}$ are indicated. There is an obvious tendency of the maxima of this projection to reduce their heights and blur out when x approaches $\frac{1}{2}$. Arrows connect identical maxima of the two projections. Each of the two systems of networks connects maxima due to interaction between Mo atoms of the same layer of the structure.

Patterson projection parallel to [0 0 1], p(xy), Fig. 2 a, where the y coordinates of the heavy maxima do not show any deviations from the values 0 and $\frac{1}{2}$. It may thus be supposed that *Pnma* is the actual space-group and the consistency of the structure with that symmetry will be examined.

The projection of the Patterson function parallel to [0 1 0], p(xz), is represented in Fig. 2 b. Most maxima of this function occur at points forming two congruent interpenetrating networks, indicated in the figure by full and dotted lines. The side lengths of the unit mesh are about 3.8 and 2.6 Å. These values agree with the probable lengths of the space diagonal and the side of a regular MoO_6 octahedron. The following structure scheme based on these observations is consistent with the heavy maxima of p(xz) and p(xy) *:

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* Notations according to *International tables for the determination of crystal structures* Berlin (1935).

4 Mo_1 in 4(c):	$\frac{x_A}{2}$	$\frac{3}{4}$	$\frac{1 + z_A}{2}$
4 Mo_2 in 4(c):	$\frac{x_A + x_B}{2}$	$\frac{1}{4}$	$\frac{z_A + z_B}{2}$
4 Mo_3 in 4(c):	$\frac{x_B + x_C}{2}$	$\frac{3}{4}$	$\frac{z_B + z_C}{2}$
4 Mo_4 in 4(c):	$\frac{x_C + x_D}{2}$	$\frac{1}{4}$	$\frac{z_C + (z_D - 1)}{2}$

For moderately high values of h and l these metal positions give F^2_{h0l} values in harmony with the observed ones. The Mo coordinates could be improved from a few successive calculations of the electron density projection $\varrho(xz)$. It was then possible to obtain the sign of the structure factor of most reflections $h\ k\ l$ with a high degree of certainty, the influence of the O atoms in general being too small to be of any importance compared with the contribution of the metal atoms. The positions of the Mo atoms were definitely settled from the cut $\varrho(x\,\frac{1}{4}\,z)$ in the electron density function, utilizing almost all of the observed reflections. In that way the following arrangement of the Mo atoms, consistent with the symmetry *Pnma*, was obtained:

4 Mo_1 in 4(c):	0.0285	$\frac{3}{4}$	0.840
4 Mo_2 in 4(c):	0.087	$\frac{1}{4}$	0.518
4 Mo_3 in 4(c):	0.1465	$\frac{3}{4}$	0.196
4 Mo_4 in 4(c):	0.2055	$\frac{1}{4}$	0.869

The accuracy is estimated to be ± 0.001 for the x coordinates and ± 0.003 for the z coordinates.

OXYGEN POSITIONS

The projections of the Patterson function p(xy) and p(xz) contain a number of diffuse maxima that might be due to Mo-O interaction, but it was not thought possible to make any conclusions from them as to the arrangement of the O atoms. However from the disposition of the Mo atoms indexed 1—3 it seems reasonable that these atoms coordinate six O atoms in an octahedral way, the MoO_6 octahedra thus formed being joined by corners. Then each Mo_4 atom will be surrounded by four O atoms forming a tetrahedron.

If *Pnma* is the actual space-group space reasons require the O atoms to be situated in the mirror planes ($y = \frac{1}{4}$ and $\frac{3}{4}$) or approximately midway between them. The cuts $\varrho(x\ \frac{1}{4}\ z)$ and $\varrho(x\ 0\ z)$ in the electron density function might thus give information about the x and z coordinates of the O atoms.

The former cut, besides the heavy Mo maxima, shows a number of minor peaks. All those required by the proposed O arrangement are found with quite reasonable distances mutually and to the Mo positions. However, as there are also other maxima of almost the same magnitude, not explicable as being due to a possible structure and evidently caused by cutting off effects, the accuracy of the following O positions cannot be very high.

4 O_5 in 4(*c*):	0.028	$\frac{1}{4}$	0.34
4 O_6 in 4(*c*):	0.088	$\frac{3}{4}$	0.03
4 O_7 in 4(*c*):	0.163	$\frac{1}{4}$	0.67
4 O_8 in 4(*c*):	0.222	$\frac{3}{4}$	0.37

In $\varrho(x\ 0\ z)$ maxima occur which can be interpreted as due to O atoms completing the octahedra around Mo_1, Mo_2, and Mo_3 and the tetrahedron around Mo_4 and giving quite reasonable interatomic distances. A maximum at $x = 0$, $z = 0$ must correspond to O atoms occupying a fourfold position 4(*a*), as the possibility of its connection with an eightfold position 8(*d*) is excluded for space reasons. The *x* and *z* coordinates of the remaining O atoms — situated in three eightfold positions 8(*d*) — cannot be very accurate as a few rather strong accessory peaks occur in the cut. The *y* coordinates of these atoms must be close to 0 (and $\frac{1}{2}$) for space and functional reasons.

4 O_1 in 4(*a*):	0	0	0
8 O_2 in 8(*d*):	0.063	0.00	0.69
8 O_3 in 8(*d*):	0.123	0.00	0.35
8 O_4 in 8(*d*):	0.183	0.00	0.01

DESCRIPTION OF THE STRUCTURE

The following structure is thus arrived at:

Cell content: 4 Mo_4O_{11}
Space-group: D_{2h}^{16} — *Pnma*

4 Mo_1 in 4(*c*):	0.0285	$\frac{3}{4}$	0.840
4 Mo_2 in 4(*c*):	0.087	$\frac{1}{4}$	0.518
4 Mo_3 in 4(*c*):	0.1465	$\frac{3}{4}$	0.196
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4 O_8 in 4(*c*):	0.222	$\frac{3}{4}$	0.37

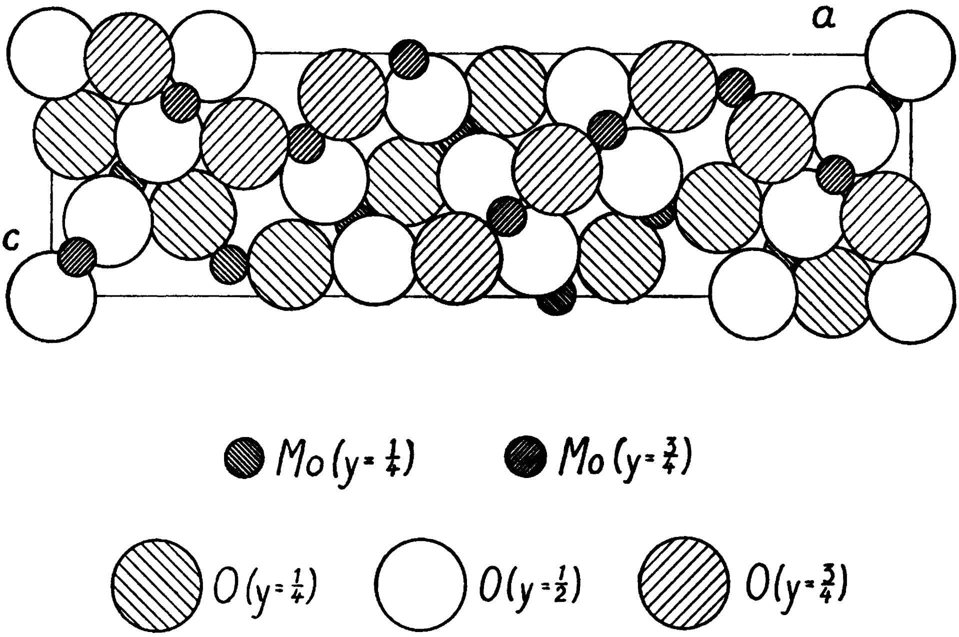

Fig. 3. Projection of the unit cell of Mo_4O_{11} *parallel to [0 1 0]. The O atoms at* $y = 1$ *are omitted.*

A projection of the elementary cell parallel to [0 1 0] is given in Fig. 3. In Table 1 a number of observed and calculated structure factor values are compared. Their agreement may be considered rather satisfactory.

The lattice may be described as consisting of layers of infinite extension normal to [1 0 0], *cf.* Fig. 4. Three fourths of the Mo atoms (Mo_1, Mo_2, and Mo_3) coordinate six O atoms to form distorted MoO_6 octahedra, which are mutually joined by corners. The rest of the Mo atoms (Mo_4) coordinate three O atoms of adjacent MoO_6 octahedra of the same layer and one O atom of the neighbouring layer to form distorted MoO_4 tetrahedra, thus bringing about the connection between the layers. The finite extension of the layers corresponds to three MoO_6 octahedra and one MoO_4 tetrahedron joined by corners, the Mo atoms of these polyhedra being situated close to a straight line. The directions of these lines are different for adjacent layers.

No difference can be observed between the Mo-Mo distances of adjacent octahedra or the corresponding distances of an octahedron and a tetrahedron. They all vary about 3.75 Å, the limiting values being 3.70 and 3.79 Å. These figures are in agreement with the Mo-Mo distances of octahedra joined by

Table 1. Weissenberg photographs with Mo-K radiation. Comparison between observed and calculated $\lvert F \rvert$ values.

h k l	$\lvert F \rvert$		h k l	$\lvert F \rvert$		h k l	$\lvert F \rvert$	
	obs.	calc.		obs.	calc.		obs.	calc.
4 0 0	50	70	13 0 2	—	10	22 0 7	100	130
6 0 0	70	80	14 0 2	50	50	23 0 7	—	60
8 0 0	70	70	15 0 2	50	30	24 0 7	—	0
10 0 0	70	70	16 0 2	—	20	16 1 0	—	40
12 0 0	60	40	17 0 2	—	10	16 2 0	520	380
14 0 0	130	120	18 0 2	—	20	16 3 0	—	40
16 0 0	250	220	19 0 2	—	10	16 4 0	310	200
18 0 0	300	250	20 0 2	—	20	16 5 0	—	30
20 0 0	—	30	21 0 2	—	10	16 6 0	350	380
22 0 0	—	50	22 0 2	140	140	16 7 0	—	30
24 0 0	—	30	23 0 2	180	200	16 8 0	240	160
26 0 0	—	20	24 0 2	140	150	26 1 0	370	300
28 0 0	—	20	25 0 2	—	20	26 2 0	—	30
30 0 0	—	30	26 0 2	—	10	26 3 0	320	290
32 0 0	—	40	27 0 2	120	180	26 4 0	—	20
34 0 0	260	280	28 0 2	160	110	26 5 0	230	260
36 0 0	—	50	29 0 2	110	170	26 6 0	—	20
0 2 0	760	530	30 0 2	—	30	26 7 0	200	230
0 4 0	720	970	1 0 7	—	10	26 8 0	—	10
0 6 0	660	420	2 0 7	—	30	34 1 0	—	0
0 8 0	480	610	3 0 7	90	90	34 2 0	330	230
0 0 2	—	20	4 0 7	210	220	34 3 0	—	0
0 0 4	70	90	5 0 7	200	220	34 4 0	330	250
0 0 6	330	470	6 0 7	—	80	34 5 0	—	0
0 0 8	—	80	7 0 7	70	100	34 6 0	270	180
0 0 10	—	30	8 0 7	—	0	34 7 0	—	0
0 0 12	—	60	9 0 7	—	10	34 8 0	260	210
1 0 2	160	100	10 0 7	—	20	1 2 2	120	80
2 0 2	—	10	11 0 7	—	20	2 2 2	120	100
3 0 2	200	120	12 0 7	120	130	3 2 2	120	130
4 0 2	—	20	13 0 7	160	170	4 2 2	120	100
5 0 2	240	180	14 0 7	70	140	5 2 2	430	320
6 0 2	240	180	15 0 7	—	20	6 2 2	440	360
7 0 2	150	120	16 0 7	—	40	7 2 2	370	220
8 0 2	120	110	17 0 7	—	10	8 2 2	100	90
9 0 2	50	40	18 0 7	—	40	9 2 2	—	10
10 0 2	300	260	19 0 7	—	30	10 2 2	210	150
11 0 2	330	360	20 0 7	—	70	11 2 2	280	250
12 0 2	150	190	21 0 7	140	110	12 2 2	150	110

Table 1 (contd.).

h k l	F obs.	F calc.	h k l	F obs.	F calc.	h k l	F obs.	F calc.
13 2 2	—	10	19 2 2	—	10	25 2 2	—	10
14 2 2	—	10	20 2 2	—	40	26 2 2	—	30
15 2 2	—	10	21 2 2	—	30	27 2 2	150	220
16 2 2	—	0	22 2 2	70	60	28 2 2	150	140
17 2 2	—	40	23 2 2	170	160	29 2 2	110	160
18 2 2	—	0	24 2 2	190	140	30 2 2	—	40

corners observed for Mo_9O_{26} and Mo_8O_{23}, the average values being 3.70 and 3.77 Å respectively [6].

The Mo-O and O-O distances cannot be very exact due to the relative inaccuracy of the O positions. The Mo-O distances within the MoO_6 octahedra vary between 1.8 and 2.2 Å with an average value of 1.91 Å. (For Mo_9O_{26} and Mo_8O_{23} the average Mo-O distances are 1.91 and 1.94 Å respectively[6].) However, there seems to be some difference between the Mo-O distances depending on whether the O atom is common to two octahedra or to one octahedron and one tetrahedron. In the former case the distances are between 1.8 and 2.0 Å, in the latter they fall in the interval 2.05 to 2.2 Å. In this way the O atoms will be closer to the Mo atoms of the tetrahedra showing Mo-O distances of about 1.75 Å. Similar values have been calculated by Sillén and Nylander [7] for the Mo-O distance of the MoO_4 group of $SrMoO_4$.

The O-O distances of the MoO polyhedra are of reasonable lengths, with values from 2.55 to 3.1 Å.

DISCUSSION OF THE STRUCTURE

The structure of Mo_4O_{11} is rather different from those of the other molybdenum oxides hitherto investigated. The occurence of MoO_4 tetrahedra in Mo_4O_{11} totally lacks analogy in these oxides which are exclusively built up by MoO_6 octahedra. The deficit in oxygen content of the lower molybdenum oxides in relation to MoO_3 is thus maintained in two quite different ways: by the presence of MoO_4 tetrahedra in Mo_4O_{11} and by the MoO_6 octahedra to a minor or greater extent sharing edges in Mo_9O_{26}, Mo_8O_{23} [6], and MoO_2 [8]. (In the latter oxide every O atom is in this way common to three octahedra.)

The structure of Mo_4O_{11} shows planes sparingly occupied by atoms, viz. the joints between the layers mentioned above. This causes a rather weak

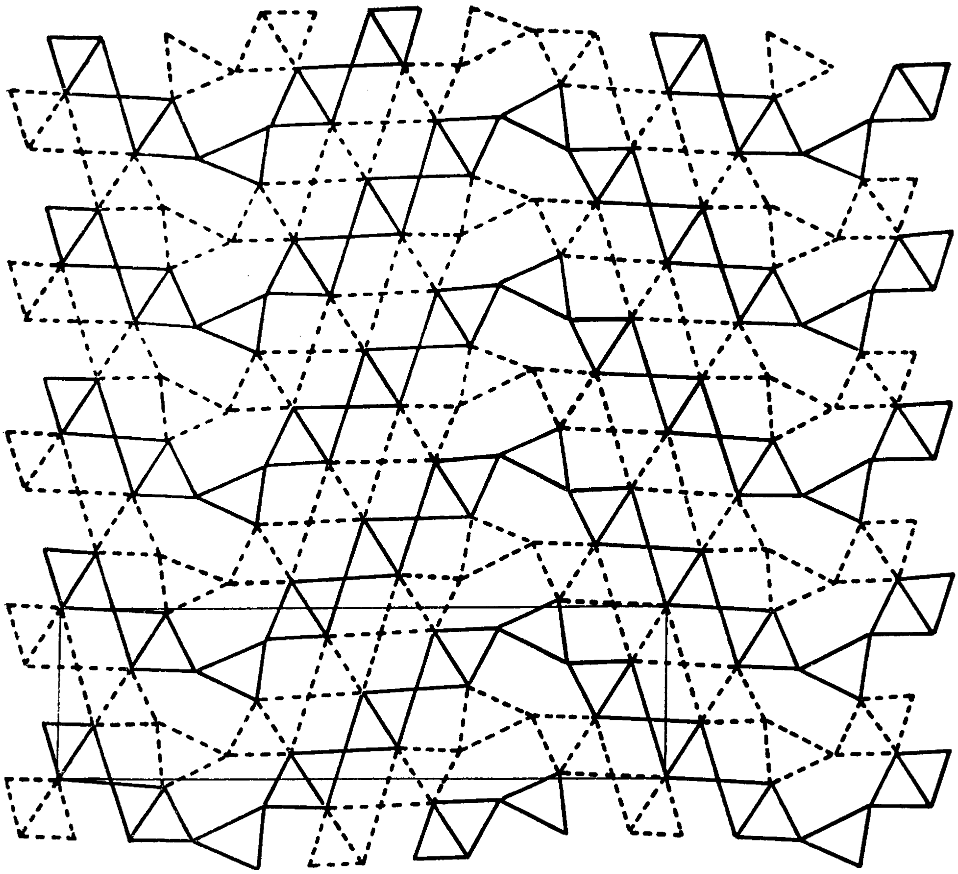

Fig. 4. Projection of the structure parallel to [0 1 0]. The extension of one unit cell is indicated. MoO_6 octahedra and MoO_4 tetrahedra, the Mo atoms of which are situated at $y = \frac{1}{4}$ and $y = \frac{3}{4}$, are indicated by dotted and full lines respectively.

cohesion in the direction of the *a* axis, which is reflected in the shape of the crystals, showing thin plates parallel to (1 0 0).

The structure of Mo_4O_{11} is a very spacious one compared with those of the other molybdenum oxides. The quotient between the volume of the unit cell and the number per cell of the bulky O atoms may to some extent be used as a measure of this property. The average space available per O atom (the volume of the small Mo atoms being neglected) for the different molybdenum oxides is listed in Table 2 as well as the corresponding figure for a hypothetical compound RO_3 of $D0_9$-type (ReO_3-type)[9] with a R-R distance of 3.75 Å. It is

Table 2. The average space available per O atom for different molybdenum oxides.

	Number of formula units per cell	Volume of the unit cell, V	V divided by the number of O atoms per cell
MoO_2	4	131.3 * Å^3	16.4 Å^3
Mo_4O_{11}	4	890	20.2
Mo_8O_{23}	2	870	18.9
Mo_9O_{26}	2	970	18.7
MoO_3	4	203.0 *	16.9
RO_3 of $D0_9$-type (ReO_3-type) R—R = 3.75 Å	1	52.7	17.6

evident that the lattices of Mo_9O_{26}, Mo_8O_{23}, and especially of Mo_4O_{11} are much more loosely packed than those of MoO_2 and MoO_3, which are even more compact than the hypothetical RO_3 lattice. However, while the bulkiness of the structures of Mo_9O_{26} and Mo_8O_{23} is due to the deformation of the MoO_6 octahedra, being lengthened parallel to [0 1 0], the lattice of Mo_4O_{11} contains irregularly shaped holes of appreciable size, situated in the layer joint regions. It may be that extra atoms or molecules can be inserted in these interstices. The catalytic action of »molybdenum oxides» on divers chemical reactions may be connected with these cavities.

SUMMARY

The γ-molybdenum oxide has been shown to have the composition Mo_4O_{11}. A complete structure determination has been carried out. The lattice is constructed of MoO_6 octahedra and MoO_4 tetrahedra coupled together by sharing corners. The oxide may be described as being composed of layers infinitely extended in two dimensions. The MoO_4 tetrahedra connect adjacent layers.

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* The figures given in [1] and [8], in fact expressed in kX units, are here converted into Å units.

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