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The Crystal Structures of Mo_9O_{26} (β'-Molybdenum Oxide) and Mo_8O_{23} (β-Molybdenum Oxide)

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In a previous communication from this Institute [1], the existence of two molybdenum oxides of a composition close to $MoO_{2.90}$ was reported. The one formed at about 700° C was denominated the β'-oxide, the other obtained at a maximum temperature of about 650° C was called the β-oxide. A description of the appearance of the oxides and of the method of preparing them was given in [1].

The determination of the structure has been entirely based on Weissenberg photographs taken with Mo-K radiation. The estimation of the intensities was carried out visually, starting from 4 : 2 : 1 as relative values of the intensities of Mo-$K\alpha_1$, Mo-$K\alpha_2$, and Mo-$K\beta$ radiation. Relative values of the structure amplitude were obtained by dividing the intensity values by $(1 + \cos^2 2\Theta)/\sin^2 2\Theta$. The temperature factor was neglected.

The calculations of Patterson and electron density function projections and cuts were carried out by means of the electric machine for the summation of Fourier series, constructed by Hägg and Laurent [2].

DERIVATION OF THE STRUCTURE OF Mo_9O_{26} (β'-MOLYBDENUM OXIDE)

Unit cell and space-group

A crystal suitable for taking single crystal photographs was obtained from a preparation $MoO_{2.92}$, which had been heated at 700° C for 60 hours. Laue photographs showed the Laue symmetry to be C_{2h}—$2/m$. Rotation and Weissenberg photographs were taken around [0 1 0]. By using Mo-K radiation it was then possible to obtain layer lines with $k = 0$—5. Reflections $0\ k\ l$ were

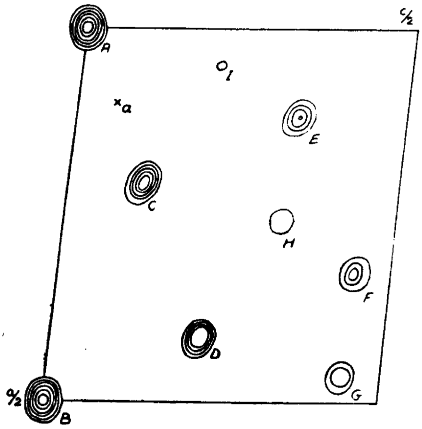

Fig. 1. Mo_9O_{26}. *Projection of the Patterson function on the ac plane, p (xz). Only maxima whose centres of gravity belong to the sketched area are indicated.*

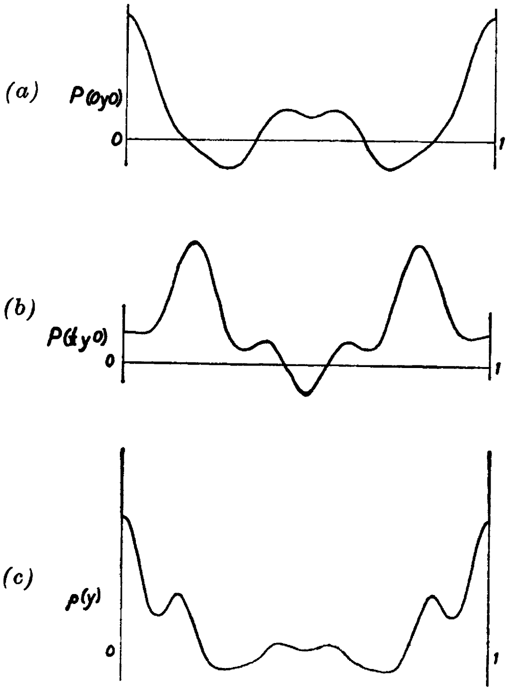

Fig. 2. Mo_9O_{26}. *The Patterson function along the lines 0,y,0 (a) and ½,y,0 (b). Projection of the Patterson function on the b axis (c).*

registered on a Weissenberg photograph with [1 0 0] as axis of rotation. This made it possible to correlate the intensity scales of the former photographs.

The dimensions of the monoclinic unit cell proved to be:

$$a = 16.75 \text{ Å},\ b = 4.03 \text{ Å},\ c = 14.45 \text{ Å},\ \beta = 96°$$

The volume of the unit cell is 970 $Å^3$. The density value, 4.26, obtained for a preparation evidently consisting of practically pure β'-molybdenum oxide ($MoO_{2.88}$ heated at 700° C for 60 hours)[1] corresponds to 17.5 $MoO_{2.88}$ units per cell. This makes it rather probable that the elementary cell contains two formula units Mo_9O_{26} (corresponding to 18 $MoO_{2.89}$). The density calculated under this assumption would be 4.38.

Reflections $h\ 0\ l$ only appear when h is even. Reflections $0\ k\ 0$ are present in all the orders. Thus one of the space-groups C_s^2—Pa and C_{2h}^4—$P2/a$ is probable. The investigation was started by examining whether the structure was consistent with the latter space-group, having the higher symmetry.

Molybdenum positions

From the F^2_{h0l} values the projection of the Patterson function on the *ac* plane, p(xz), was calculated (Fig. 1 and Table 1). The projection obtained shows a rather smooth background with discrete maxima rising from it. As the *b* axis of the unit cell is quite short it seems probable that the background corresponds to the p(xz) value zero. The height of a maximum above this lowest level may be looked upon as an approximate measure of its magnitude.

The shortness of the *b* axis excludes the possibility of two Mo atoms having the same x and z coordinates, which may also be inferred from the fact that the cut P(0 y 0) in the Patterson function (Fig. 2 a) only contains the single strong maximum at $y = 0$. The major peaks B—G of p(xz) are presumably chiefly due to Mo—Mo vectors and may all be interpreted as effected by 18 Mo atoms arranged according to one of the following alternatives *:

Alternative I.

2 Mo_1 in 2(*a*) or 2(*c*):	$0\ 0\ 0$ or $0\ \frac{1}{2}\ 0$
4 Mo_2 in 4(*g*):	$x_C\ y_2\ z_C$
4 Mo_3 in 4(*g*):	$x_D\ y_3\ z_D$
4 Mo_4 in 4(*g*):	$x_E\ y_4\ z_E$
4 Mo_5 in 4(*g*):	$x_F\ y_5\ z_F$

Alternative II.

2 Mo_1 in 2(*e*):	$\frac{1}{4}\ y_1\ 0$
4 Mo_2 in 4(*g*):	$(x_C + \frac{1}{4})\ y_2\ z_C$
4 Mo_3 in 4(*g*):	$(x_D - \frac{1}{4})\ y_3\ z_D$
4 Mo_4 in 4(*g*):	$(x_E + \frac{1}{4})\ y_4\ z_E$
4 Mo_5 in 4(*g*):	$(x_F - \frac{1}{4})\ y_5\ z_F$

The Mo positions of these two alternatives differ essentially with regard to the twofold axes. It is not possible to decide between them from reflections $h\,0\,l$.

The consistency of the Patterson function generated by the proposed Mo arrangements (Alternatives I and II) with the projection calculated from the F^2_{h0l} values, p(xz), appears from Table 1. The heights above the background level of the maxima of p(xz) agree rather well with those required by the metal atom lattices although they comprise Mo—O and O—O maxima. Two further maxima, H and I, required by the proposed structures and corresponding to 6 and 4 Mo—Mo vectors respectively, are found at the calculated positions. A remaining maximum due to 2 Mo—Mo vectors could not, however, be observed with certainty.

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* Notations analogous to those of space-group C^4_{2h} — $P\ 2/c$ in *International tables for the determination of crystal structures.* Berlin (1935).

Table 1. Mo_9O_{26}. *Projection of the Patterson function on the ac plane, p(xz).*

Maximum Cf. Fig. 1	Coordinates observed		Number of Mo—Mo vectors estimated from p(xz) (The influence of the O atoms being neglected.)	Number of Mo—Mo vectors required by the structures proposed.
	x	z		
A	0	0	18	18
B	$\frac{1}{2}$	0	18	18
C	0.208	0.113	14.8	16
D	0.413	0.225	12.5	14
E	0.123	0.337	12.0	12
F	0.327	0.448	10.2	10
G	0.466	0.440	8.8	8
H	0.257	0.328	7.5	6
I	0.050	0.209	6.3	4
—				
a (Mo—O vector)	0.10	0.058	—	—

F^2_{h0l} values calculated on the basis of the proposed structures are in good agreement with the observed values for reflections with moderately high indices. The $\varrho(xz)$ functions for the two alternative structures estimated from these F_{h0l} values contain 18 heavy peaks with only slight deviations from the assumed Mo positions. A repeated computation of the $\varrho(xz)$ functions with F_{h0l} values based on the coordinates thus obtained gives two sets of x and z parameters for Mo which bring about good agreement between observed and calculated F^2_{h0l}.

The two following alternatives of distributing the Mo atoms are thus possible:

Alternative I.

2 Mo_1 in 2(*a*) or 2(*c*):	0 0 0 or 0 $\frac{1}{2}$ 0		
4 Mo_2 in 4(*g*):	0.206	y_2	0.113
4 Mo_3 in 4(*g*).	0.412	y_3	0.221
4 Mo_4 in 4(*g*):	0.119	y_4	0.334
4 Mo_5 in 4(*g*):	0.332	y_5	0.450

Alternative II.

2 Mo_1 in 2(*e*):	$\frac{1}{4}$	y_1	0
4 Mo_2 in 4(*g*):	0.456	y_2	0.113
4 Mo_3 in 4(*g*):	0.162	y_3	0.221
4 Mo_4 in 4(*g*):	0.369	y_4	0.334
4 Mo_5 in 4(*g*):	0.082	y_5	0.456

The error in the parameter values is estimated to be ± 0.002 corresponding to about ± 0.03 Å.

The vectors caused by Mo atoms mutually connected by means of the glide plane must correspond to maxima in the Patterson function on a line perpendicular to the *ac* plane and cutting this plane in $x = \frac{1}{2}$, $z = 0$. The appearance of $P(\frac{1}{2}\ y\ 0)$ is given in Fig. 2 b. The major peaks at $y = 0.18$ and $y = 0.82$ are evidently due to Mo—Mo vectors. The corresponding Mo atoms must lie in planes normal to the *b* axis and $0.18b$ apart symmetrically to the glide planes, *i. e.* in $y = \pm\ 0.09$ or in $y = (\frac{1}{2} \pm 0.09)$. If there are Mo atoms in both of these sets of planes there must be a maximum in the projection of the Patterson function on the *b* axis, $p(y)$, at $y \approx 0.32$. As such a maximum is totally lacking (Fig. 2 c) only one of the double planes ought to contain Mo atoms. The parameter values $y = 0.41$ and $y = 0.59$ are arbitrarily chosen for these atoms. The comparatively high value of $P(\frac{1}{2}\ y\ 0)$ at $y = 0$ might possibly indicate that one of the Mo positions, corresponding to two or four Mo atoms, has the *y* parameter close to 0 or 0.5. This possibility cannot be excluded from the appearance of $p(y)$. However, an arrangement with two or four Mo atoms near the plane $y = 0$ and the other ones equally distributed at $y = 0.41$ and 0.59 does not give calculated values of F^2_{0k0} compatible with the observed ones.

The establishment of the arrangement of the Mo atoms with respect to the remaining *y* parameter values (0.41, $\sim$ 0.50, 0.59) may be carried out by examining reflections $h\ k\ l$ with *h* odd, as those with *h* even are not influenced by the distribution of the Mo atoms in the planes $y = 0.41$ and $y = 0.59$. In this way it is possible to decide between the proposed arrangements of the metal atoms, Alternatives I and II. The F^2_{hkl} values are computed for a number of reflections $h\ k\ l$ ($h =$ odd) for the following alternatives:

Alternative I. The twofold Mo position has $y = \frac{1}{2}$ (corresponding to 2(*c*)); the other Mo positions are given the *y* parameters 0.41 and 0.59 in all arrangements.

Alternative II. a) All arrangements of one Mo position (two- or fourfold) at $y = 0.50$, the others at $y = 0.41$ and 0.59.

b) All arrangements of the Mo positions at $y = 0.41$ and 0.59.

Conformity between observed and calculated F^2_{hkl} is only obtainable for one of these arrangements (belonging to Alternative II b). The Mo atoms of the oxide thus have positions with the symmetry C^4_{2h}—$P2/a$, *x* and *z* coordinates equal to those given above for Alternative II and the following *y* parameters:

$$y(\mathrm{Mo}_1) = 0.59,\quad y(\mathrm{Mo}_2) = 0.41,\quad y(\mathrm{Mo}_3) = 0.41,$$
$$y(\mathrm{Mo}_4) = 0.59,\quad y(\mathrm{Mo}_5) = 0.41.$$

The error in the y parameters is probably less than ± 0.01 corresponding to about ± 0.04 Å.

The sign of most F_{hkl} values can be determined from this Mo arrangement as the influence of the Mo atoms in most cases dominates over the contribution of the O atoms.

By examining the electron density function (ϱ) along lines normal to the *ac* plane and cutting it in $x = x(\mathrm{Mo})$ and $z = z(\mathrm{Mo})$ it is possible to verify the $y(\mathrm{Mo})$ parameters. This was done for $\mathrm{Mo_1}$ and $\mathrm{Mo_5}$. The curves show heavy maxima at the y values arrived at above. However it seems impossible to correct the y coordinates in this way owing to the low number of Fourier terms in the y direction, the maximum value of k being 5.

Oxygen positions

In the Patterson projection on the *ac* plane (Fig. 1) there are a number of minor peaks not interpretable as projections of Mo—Mo vectors and thus probably due to Mo—O interaction. The vector projection Aa, halving the projected Mo—Mo distance AC, may indicate O atoms situated between such adjacent Mo atoms of the structure. Thus it seems reasonable that a number of O atoms are located in or close to the plane $y = \frac{1}{2}$. From a computation of the electron density function in this plane, $\varrho(x\,\frac{1}{2}\,z)$, it appears that besides maxima caused by the proximity of the Mo atoms, there are minor maxima, evidently due to O atoms at the following points:

2 $\mathrm{O_6}$	in 2(c):	0	$\frac{1}{2}$	0
4 $\mathrm{O_7}$	in 4(g):	0.355	0.50	0.06
4 $\mathrm{O_8}$	in 4(g):	0.21	0.50	0.115
4 $\mathrm{O_9}$	in 4(g):	0.06	0.50	0.18
4 $\mathrm{O_{10}}$	in 4(g):	0.42	0.50	0.23
4 $\mathrm{O_{11}}$	in 4(g):	0.26	0.50	0.285
4 $\mathrm{O_{12}}$	in 4(g):	0.125	(<) 0.50	0.345
4 $\mathrm{O_{13}}$	in 4(g):	0.465	~0.50	0.42
4 $\mathrm{O_{14}}$	in 4(g):	0.32	~0.50	0.46

The $y(\mathrm{O})$ values are arrived at in the following way. For space reasons it is evident that the $\mathrm{O_6}$ atom at $x = 0$, $z = 0$ must occupy a twofold position and thus be situated in 2(c): $0\,\frac{1}{2}\,0$. All the O maxima in $(x\,\frac{1}{2}\,z)$ are of the same magnitude, indicating that the atoms are located fairly close to the plane $y = \frac{1}{2}$. Similar to $\mathrm{O_6}$ the O atoms indexed 7—11 seem to constitute the corners shared by two Mo—O polyhedra with the Mo atoms symmetrically displaced in relation to $y = \frac{1}{2}$. This makes it probable that the y parameters of these O atoms are equal to 0.50. $\mathrm{O_{12}}$ is situated between two Mo atoms with $y = 0.41$, and $y(\mathrm{O_{12}})$ might for that reason be somewhat less than 0.50. The y values of $\mathrm{O_{13}}$ and $\mathrm{O_{14}}$ cannot be easily corrected from similar considerations.

The Patterson function curves $P(0\ y\ 0)$ and $P(\frac{1}{2}\ y\ 0)$ (Fig. 2 a and b) show minor peaks at $y \approx 0.4$ and $y \approx 0.6$ besides the main peaks due to Mo—Mo vectors. If these maxima are generated by Mo—O interaction, which seems probable, they would indicate O atoms having about the same x and z coordinates as a number of Mo atoms and located near the planes $y = 0.8$ or $y = 0$. The former possibility, however, is definitely excluded from considerations of space as it would give much too short O—O distances. The cut $\varrho(x\ 0\ z)$ in the electron density function contains maxima at points with the x and z coordinates arrived at for the Mo atoms. These peaks are higher than those corresponding to oxygen in $\varrho(x\ \frac{1}{2}\ z)$, evidently due to the influence of the Mo atoms. However, the maxima do not show any trace of distortion indicating a difference between the x and z coordinates of molybdenum and oxygen. Linear cuts through these points normal to the ac plane, for instance $\varrho(\frac{1}{4}\ y\ 0)$, are influenced by cutting off effects so that the correction of the y(O) coordinates has to be carried out from considerations of space.

The average distance between Mo atoms and neighbouring O atoms close to the plane $y = \frac{1}{2}$ amounts to 1.91 Å. If one assumes the shortest distance between Mo atoms and O atoms at $y \approx 0$ to have about the same value, these O atoms must have the y parameters equal to y(Mo) + 0.47, giving the shortest O—O distance a value of 2.5 Å. Thus the following O positions are obtained:

2 O_1	in $2(e)$:	$\frac{1}{4}$	0.06	0
4 O_2	in $4(g)$:	0.455	0.94	0.115
4 O_3	in $4(g)$:	0.16	0.94	0.22
4 O_4	in $4(g)$:	0.37	0.06	0.335
4 O_5	in $4(g)$:	0.08	0.94	0.45

Final structure of Mo_9O_{26}

It is thus possible to describe the arrangement of the atoms of the oxide in the following manner:

Cell content: $2Mo_9O_{26}$.

Space group : C_{2h}^4 — $P\ 2/a$.

2 Mo_1	in $2(e)$:	$\frac{1}{4}$	0.59	0
4 Mo_2	in $4(g)$:	0.456	0.41	0.113
4 Mo_3	in $4(g)$:	0.162	0.41	0.221
4 Mo_4	in $4(g)$:	0.369	0.59	0.334
4 Mo_5	in $4(g)$:	0.082	0.41	0.450
2 O_1	in $2(e)$:	$\frac{1}{4}$	0.06	0
4 O_2	in $4(g)$:	0.455	0.94	0.155
4 O_3	in $4(g)$:	0.16	0.94	0.22
4 O_4	in $4(g)$:	0.37	0.06	0.335
4 O_5	in $4(g)$:	0.08	0.94	0.45
2 O_6	in $2(c)$:	0	$\frac{1}{2}$	0
4 O_7	in $4(g)$:	0.355	0.50	0.06
4 O_8	in $4(g)$:	0.21	0.50	0.115
4 O_9	in $4(g)$:	0.06	0.50	0.18
4 O_{10}	in $4(g)$:	0.42	0.50	0.23
4 O_{11}	in $4(g)$:	0.26	0.50	0.285
4 O_{12}	in $4(g)$:	0.125	(<)0.50	0.345
4 O_{13}	in $4(g)$:	0.465	~0.50	0.42
4 O_{14}	in $4(g)$:	0.32	~0.50	0.46

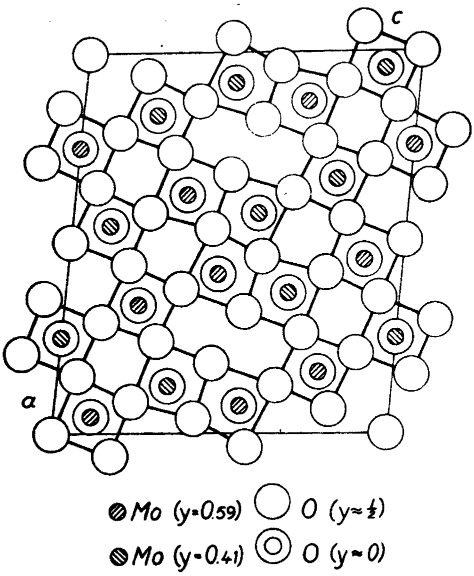

Fig. 3. Mo_9O_{26}. *Projection of the structure parallel to* [*0 1 0*].

A projection of the structure parallel to [0 1 0] is given in Fig. 3. The structure factors of a large number of reflections have been computed, some of them being given in Table 2. The agreement between observed and calculated F values is not perfect in every detail but may be looked upon as satisfactory considering the great number of parameters.

DERIVATION OF THE STRUCTURE OF Mo_8O_{23} (β-MOLYBDENUM OXIDE)

The method for the determination of the structure of Mo_8O_{23} has to some extent been analogous to the manner of solving the structure of Mo_9O_{26} and will therefore be reported briefly.

Unit cell and space-group

From a preparation $MoO_{2.90}$, which had been heated at 650° C for 24 hours, a minute needle-shaped single crystal was picked out. Laue photographs showed the Laue symmetry to be C_{2h}—$2/m$, with the digonal axis parallel to the needle axis. Rotation and Weissenberg photographs were taken with Mo-K radiation and rotation around this axis. In this way layer lines with $k = 0$—5 were registered. It was not possible to find a crystal suitable for taking photographs around another axis. Correlation between the intensity

Table 2. Mo_9O_{26}. *Weissenberg photographs with Mo-K radiation. Comparison between observed and calculated* $|F|$ *values.*

h k l	|F|		*h k l*	|F|		*h k l*	|F|	
	obs.	calc.		obs.	calc.		obs.	calc.
4 0 0	200	200	4 5 0	120	80	5 2 $\bar{8}$	130	120
6 0 0	—	60	5 5 0	—	20	5 2 $\bar{7}$	190	140
8 0 0	—	0	6 5 0	—	60	5 2 $\bar{6}$	120	100
10 0 0	300	300	7 5 0	—	40	5 2 $\bar{5}$	360	240
12 0 0	—	60	8 5 0	—	0	5 2 $\bar{4}$	350	230
14 0 0	—	10	9 5 0	—	20	5 2 $\bar{3}$	160	120
16 0 0	—	10	10 5 0	170	120	5 2 $\bar{2}$	—	40
18 0 0	—	80	0 0 4 —	—	< 50	5 2 $\bar{1}$	—	40
4 1 0	160	100	— 0 0 8			5 2 1	130	140
5 1 0	—	60	0 0 9	470	590	5 2 2	200	140
6 1 0	—	50	0 0 10—	—	< 70	5 2 3	130	120
7 1 0	180	130	— 0 0 17			5 2 4	230	230
8 1 0	—	0	0 0 18	230	340	5 2 5	230	230
9 1 0	—	70	0 1 0	450	680	5 2 6	140	130
10 1 0	260	180	0 1 1 —	—	< 40	5 2 7	—	50
11 1 0	—	70	— 0 1 8			5 2 8	—	10
12 1 0	—	50	0 1 9	360	370	5 2 9	—	50
4 2 0	100	70	0 1 10—	—	< 60	5 2 10	—	100
5 2 0	90	100	— 0 1 17			10 0 $\overline{10}$	330	310
6 2 0	—	30	0 1 18	210	240	10 0 $\bar{9}$	200	200
7 2 0	280	230	0 2 0	360	460	10 0 $\bar{8}$	—	30
8 2 0	—	0	0 2 1 —	—	< 30	10 0 $\bar{7}$	—	60
9 2 0	140	150	— 0 2 8			10 0 $\bar{6}$	—	40
10 2 0	120	130	0 2 9	200	250	10 0 $\bar{5}$	—	50
11 2 0	100	120	0 2 10—	—	< 40	10 0 $\bar{4}$	—	70
12 2 0	—	30	— 0 2 17			10 0 $\bar{3}$	—	80
4 3 0	—	20	0 2 18	120	150	10 0 $\bar{2}$	90	160
5 3 0	—	70	0 3 0 —	—	<40	10 0 $\bar{1}$	350	410
6 3 0	—	20	— 0 3 18			10 0 1	—	60
7 3 0	240	180	0 4 0	130	170	10 0 2	—	10
8 3 0	—	0	0 4 1 —	—	< 30	10 0 3	—	30
9 3 0	120	120	— 0 4 8			10 0 4	—	20
10 3 0	—	10	0 4 9	150	190	10 0 5	—	30
4 4 0	—	60	0 5 0	260	250	10 0 6	—	90
5 4 0	—	60	0 5 1 —	—	< 50	10 0 7	120	150
6 4 0	—	40	— 0 5 8			10 0 8	280	300
7 4 0	130	150	0 5 9	270	250	10 0 9	130	190
8 4 0	—	0	0 6 0	230	240	10 0 10	—	10
9 4 0	90	110	5 2 $\overline{10}$	—	60			
10 4 0	90	80	5 2 $\bar{9}$	110	100			

scales of the Weissenberg photographs had for that reason to be obtained from the estimated intensity values of reflections, belonging to the several layer lines, registered under similar conditions on the same film.

A rather small interval of oscillation was chosen, where good reflections had been observed in all the layer lines. Successive, equally exposed equi-inclination Weissenberg photographs were taken with oscillation within this interval, the film being moved a little between the exposures in order to get the resulting short Weissenberg photographs separated on the film. The influence of possible variations of the X-ray intensity from the ion tube used was reduced by repeating the sequence of exposures several times, the film being carefully adjusted to the exact position for each layer line.

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

$$a = 16.8 \text{ Å}, \quad b = 4.04 \text{ Å}, \quad c = 13.4 \text{ Å}, \quad \beta = 106°\,5$$

The volume of the unit cell is 870 Å^3. For a preparation $MoO_{2.90}$, heated at 650° C for 24 hours, Hägg determined a density of 4.32 *. This corresponds to 15.9 $MoO_{2.9}$ units per cell. Thus a cell content of two formula units Mo_8O_{23} (= 16 $MoO_{2.875}$) is very probable, giving a calculated density of 4.33.

In the Weissenberg photographs all reflections $h\ 0\ l$ with h odd are missing. This is characteristic of the space-groups C_s^2—$P\ a$, C_{2h}^4—$P\ 2/a$, and C_{2h}^5—$P\ 2_1/a$. As reflections $0\ k\ 0$ were not registered it was impossible to use these reflections to decide between the last group and the other two. However, the existence of a twofold screw axis in the structure would cause a number of heavy maxima to appear in the Patterson cut $P(x\,\frac{1}{2}\,z)$, corresponding to vectors between Mo atoms, mutually connected by the axis. For a set of reflections $h\ k\ l$ with h and l constant the F^2 values vary regularly with k to give an approximately smooth curve with a minimum at $k = 3$ for h even and a maximum at $k = 3$ for h odd. Thus the amplitudes of the Fourier series representing $P(x\,\frac{1}{2}\,z)$, $\sum_k F^2_{hkl} \cos 2\pi \frac{k}{2} = \sum_k (-1)^k F^2_{hkl}$, cannot reach any greater values. Heavy maxima will be lacking in this cut and the structure cannot contain twofold screw axes. The possibility of describing the structure by means of $C_{2h}^4 - P\,2/a$ having the higher symmetry of the two remaining space-groups will thus be examined.

Molybdenum positions

The appearance of the Patterson projection on the ac plane, $p(xz)$, is given in Fig. 4. As in Mo_9O_{26} the shortness of the b axis forbids more than one Mo atom having the same x and z coordinates. The heavy maxima of the projec-

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* According to a private communication.

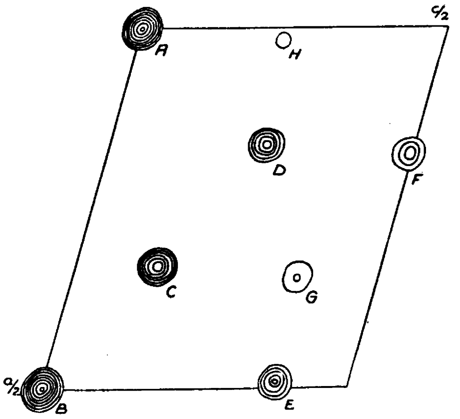

Fig. 4. Mo_8O_{23}. *Projection of the Patterson function on the ac plane, p (xz). Only maxima whose centres of gravity belong to the sketched area are indicated.*

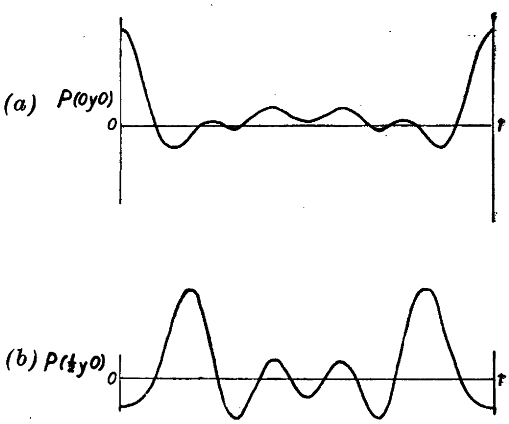

Fig. 5. Mo_8O_{23}. *The Patterson function along the lines 0y0 (a) and ½y0 (b).*

tion, B—F, are likely to depend chiefly on Mo—Mo vectors. It is possible to interpret them as caused by 16 Mo atoms arranged in two ways, which are different with regard to the distribution of the metal atoms around the digonal axes *.

Alternative I.

4 Mo_1 in 4(*g*):	$\frac{x_B + x_C}{2}$	y_1	$\frac{z_B + z_C}{2}$
4 Mo_2 in 4(*g*):	$\frac{x_C + x_D}{2}$	y_2	$\frac{z_C + z_D}{2}$
4 Mo_3 in 4(*g*):	$\frac{x_D + (x_E - \frac{1}{2})}{2}$	y_3	$\frac{z_D + z_E}{2}$
4 Mo_4 in 4(*g*):	$\frac{x_E + x_F}{2}$	y_4	$\frac{z_E + z_F}{2}$

Alternative II. Four fourfold Mo positions (*g*) with x parameters differing from those of Alternative I by ½, while the z parameters are unchanged.

A comparison between the Patterson function required by the proposed alternative structures and the calculated projection p(xz) shows the conformity

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* Notations analogous to those of space-group C_{2h}^4 — $P2/c$ in *International tables for the determination of crystal structures.* Berlin (1935).

to be as good as for Mo_9O_{26}. The weak maxima G and H correspond to 6 and 4 Mo—Mo distances whereas another maximum corresponding to 2 Mo—Mo vectors is not recognized with certainty. The agreement between calculated and observed F^2_{h0l} is also satisfactory for moderately high values of h and l. After two successive computations of the projection of the ϱ function on the *ac* plane, $\varrho(xz)$, the following corrected x and z parameters of the Mo positions are arrived at:

	Alternative I.		*Alternative II.*	
	x	z	x	z
Mo_1	0.415	0.063	0.165	0.063
Mo_2	0.246	0.188	0.496	0.188
Mo_3	0.077	0.316	0.327	0.316
Mo_4	0.404	0.445	0.154	0.445

The error in the parameter values may be ± 0.002 corresponding to about ± 0.03 Å.

The appearance of the linear Patterson cut $P(\frac{1}{2}\,y\,0)$ is given in Fig. 5 b. There are high maxima at $y = 0.18$ and $y = 0.82$, evidently due to Mo—Mo interaction. The Mo atoms must therefore be arranged in planes normal to the b axis and 0.18 b apart, symmetrically to the glide planes, *i. e.* in $y = \pm 0.09$ and $y = (\frac{1}{2} \pm 0.09)$. However, an examination of a few reflections $0\,k\,l$ shows that only one of these double planes can be occupied by Mo atoms. In order to get conformity with Mo_9O_{26} the y parameters 0.41 and 0.59 are chosen. By arranging these coordinate values on the Mo positions of Alternatives I and II in all possible ways and comparing the corresponding calculated F^2_{hkl} values with the observed ones for a number of reflections with h odd it is found that only the following arrangement according to Alternative I, will give satisfactory agreement:

$$y(Mo_1) = 0.59, \quad y(Mo_2) = 0.41, \quad y(Mo_3) = 0.59, \quad y(Mo_4) = 0.41$$

The error in these parameters may hardly exceed ± 0.01 corresponding to ± 0.04 Å.

Oxygen positions

In the Patterson cuts $P(0\,y\,0)$ and $P(\frac{1}{2}\,y\,0)$, Fig. 5 a and b, minor maxima occur at $y \approx 0.4$ and $y \approx 0.6$, evidently analogous to the Mo — O maxima of the corresponding cuts of Mo_9O_{26}. The cuts in the electron density function

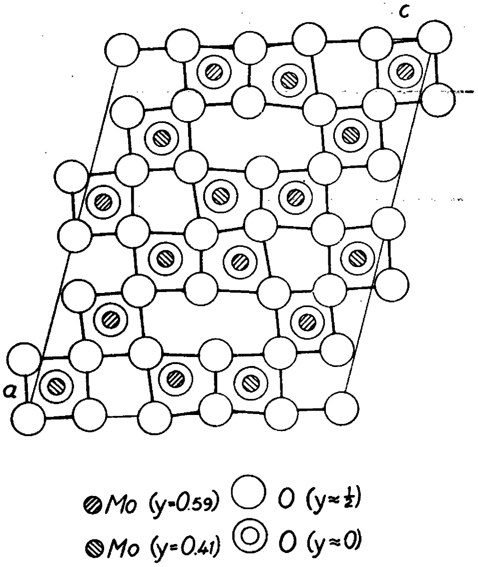

Fig. 6. Mo_8O_{23}. *Projection of the structure parallel to* [*0 1 0*].

$\varrho(x\,\frac{1}{2}\,z)$ and $\varrho(x\,0\,z)$ actually show maxima which could be interpreted as due to the O atoms. The y(O) parameters could to some extent be adjusted from functional and space reasons as was done for Mo_9O_{26}.

Final structure of Mo_8O_{23}

The structure of the oxide may thus be described in the following way:

Cell content: 2 Mo_8O_{23}.

Space group: $C_{2h}^4 - P\ 2/a$.

4 Mo_1	in 4(g):	0.415	0.59	0.063
4 Mo_2	in 4(g):	0.246	0.41	0.188
4 Mo_3	in 4(g):	0.077	0.59	0.316
4 Mo_4	in 4(g):	0.404	0.41	0.445
4 O_1	in 4(g):	0.415	0.06	0.065
4 O_2	in 4(g):	0.245	0.94	0.19
4 O_3	in 4(g):	0.075	0.06	0.315
4 O_4	in 4(g):	0.405	0.94	0.445
2 O_5	in 2(c):	0	$\frac{1}{2}$	0
4 O_6	in 4(g):	0.165	0.50	0.065
4 O_7	in 4(g):	0.335	0.50	0.135
4 O_8	in 4(g):	0.495	0.50	0.195
4 O_9	in 4(g):	. 0.17	0.50	0.27
4 O_{10}	in 4(g):	0.325	(<)0.50	0.325
4 O_{11}	in 4(g):	0.005	~0.50	0.405
4 O_{12}	in 4(g):	0.16	~0.50	0.46

A projection of the structure parallel to [0 1 0] is reproduced in Fig. 6. Part of the structure factor values computed for the structure are given in Table 3 together with the observed F values. Considering the great number of parameters the agreement may be looked upon as satisfactory.

Table 3. Mo_8O_{23}. *Weissenberg photographs with Mo-K radiation. Comparison between observed and calculated* $|F|$ *values.*

h k l	|F|		*h k l*	|F|		*h k l*	|F|	
	obs.	calc.		obs.	calc.		obs.	calc.
4 0 0	110	120	11 3 0	40	50	0 1 9	—	<30
6 0 0	390	430	12 3 0	—	10	0 1 12		
8 0 0	—	0	13 3 0	80	100	0 2 4	—	<20
10 0 0	110	90	14 3 0	—	0	0 2 7		
12 0 0	540	450	15 3 0	190	160	0 2 8	250	200
14 0 0	—	20	16 3 0	—	10	0 2 9	—	<30
16 0 0	—	50	4 4 0	—	30	0 2 12		
4 1 0	60	60	5 4 0	—	0	0 3 4	—	<20
5 1 0	—	0	6 4 0	270	230	0 3 7		
6 1 0	140	180	7 4 0	90	70	0 3 8	40	50
7 1 0	40	60	8 4 0	—	0	0 3 9	—	<30
8 1 0	—	0	9 4 0	190	140	0 3 12		
9 1 0	90	110	10 4 0	40	40	0 4 4	—	<30
10 1 0	—	50	11 4 0	—	40	0 4 7		
11 1 0	—	30	12 4 0	70	110	0 4 8	160	160
12 1 0	300	310	13 4 0	60	80	0 4 9	—	<30
13 1 0	—	60	14 4 0	—	10	0 4 12		
14 1 0	—	10	15 4 0	160	140	0 5 4	—	<30
15 1 0	70	100	16 4 0	—	20	0 5 7		
16 1 0	—	40	4 5 0	—	40	0 5 8	230	240
4 2 0	60	40	5 5 0	—	0	0 5 9	—	<40
5 2 0	—	0	6 5 0	340	270	0 5 12		
6 2 0	120	140	7 5 0	—	20	9 2 $\overline{10}$	100	110
7 2 0	110	110	8 5 0	—	0	9 2 $\bar{9}$	80	80
8 2 0	—	0	9 5 0	60	30	9 2 $\bar{8}$	200	200
9 2 0	160	200	10 5 0	60	50	9 2 $\bar{7}$	110	160
10 2 0	—	30	11 5 0	—	10	9 2 $\bar{6}$	—	50
11 2 0	40	60	12 5 0	200	160	9 2 $\bar{5}$	—	40
12 2 0	210	220	13 5 0	—	20	9 2 $\bar{4}$	130	100
13 2 0	110	120	14 5 0	—	10	9 2 $\bar{3}$	110	140
14 2 0	—	10	15 5 0	—	30	9 2 $\bar{2}$	130	150
15 2 0	160	190	16 5 0	—	30	9 2 $\bar{1}$	110	130
16 2 0	—	20	0 0 4	—	<40	9 2 1	140	180
4 3 0	—	10	0 0 7			9 2 2	70	80
5 3 0	—	0	0 0 8	480	490	9 2 3	—	10
6 3 0	160	110	0 0 9	—	<30	9 2 4	—	30
7 3 0	110	90	0 0 12			9 2 5	130	110
8 3 0	—	0	0 1 4	—	<20	9 2 6	120	140
9 3 0	180	170	0 1 7			9 2 7	120	120
10 3 0	—	10	0 1 8	270	310	9 2 8	140	160

Table 3 (contd.).

h k l	|F|		*h k l*	|F|		*h k l*	|F|	
	obs.	calc.		obs.	calc.		obs.	calc.
9 2 9	140	150	10 0 $\bar{4}$	60	60	10 0 4	60	90
9 2 10	60	80	10 0 $\bar{3}$	270	260	10 0 5	180	190
10 0 $\overline{10}$	300	420	10 0 $\bar{2}$	520	370	10 0 6	310	240
10 0 $\bar{9}$	180	120	10 0 $\bar{1}$	180	130	10 0 7	80	90
10 0 $\bar{8}$	80	60	10 0 1	80	60	10 0 8	50	70
10 0 $\bar{7}$	—	40	10 0 2	—	50	10 0 9	—	50
10 0 $\bar{6}$	—	40	10 0 3	40	50	10 0 10	—	40
10 0 $\bar{5}$	—	40						

DISCUSSION OF THE STRUCTURES

Mo_9O_{26} and Mo_8O_{23} are both built up of MoO_6 octahedra. The structures may formally be described as constructed of two-dimensional »boards», formed by MoO_6 octahedra sharing corners. (*Cf.* also the idealized structures in Fig. 7, which are further discussed later.) The boards are of infinite length parallel to the *b* axis but have an extension normal to the *b* axis of 9 octahedra for Mo_9O_{26} and 8 octahedra for Mo_8O_{23}. The two extreme octahedra of both ends of a board share edges with the corresponding octahedra of other boards. As to the rest, parallel boards are joined by octahedra sharing corners. In this way every unit cell at two localities will contain a characteristic group of four MoO_6 octahedra connected by sharing edges. (*Cf.* Fig. 7.) In the vana-

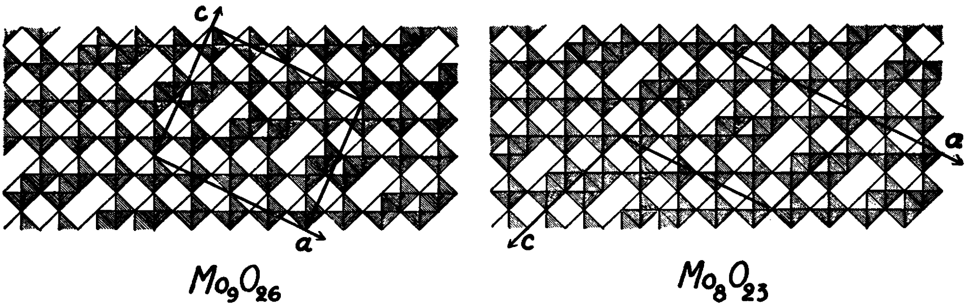

Fig. 7. Comparison between the structures of Mo_9O_{26} and Mo_8O_{23}. Idealized figures obtained by combining regular octahedra. (Mo_8O_{23} is here described on a right-handed coordinate system contrary to the other structure diagrams of this paper.)

dium oxide $V_{12}O_{26}$, investigated in this Institute by Aebi[3], a somewhat similar configuration is present.

The Mo layers parallel to (0 1 0) form a puckered network due to the Mo atoms being a little displaced mutually in the direction of the *b* axis (± 0.36 Å). The high value of the distances between adjacent Mo atoms in this direction being 4.03 Å for Mo_9O_{26} and 4.04 Å for Mo_8O_{23} is also worth mentioning. The regular alternation of the two *y* parameter values between adjacent Mo atoms is disturbed, as in the groups of four MoO_6 octahedra mentioned above the metal atoms of octahedra sharing corners have the same *y* coordinates. This arrangement is reminiscent of the distribution of the Mo atoms of the infinite zigzag shaped rows parallel to the *c* axis of MoO_3, which are also formed by MoO_6 octahedra sharing edges. In this case the mutual displacement of the Mo atoms in the direction of the *a* axis amounts to ± 0.35 Å (4) or ± 0.34 Å (5). The distance between adjacent metal atoms of different rows composing the double layers parallel to (0 1 0) is reported to be 3.954 Å (4), 3.92 Å (5), and 3.958 Å (1).

Within the network parallel to (0 1 0) the distances between Mo atoms of octahedra joined by corners for Mo_9O_{26} vary between 3.66 and 3.74 Å with an average value of 3.70 Å. For Mo_8O_{23} the corresponding limits are 3.74 and 3.82 Å and the average value 3.77 Å. The Mo atoms of octahedra joined by edges are 3.23 and 3.28 Å apart in Mo_9O_{26} and 3.23 and 3.25 Å in Mo_8O_{23}. This may be compared with the distances between Mo atoms of MoO_6 octahedra sharing edges in MoO_3, 3.42 Å (4) or 3.37 Å (5), and in MoO_2, 2.48 and 3.06 Å (6).

As the parameters of the O atoms are rather approximate the Mo—O and O—O distances of the structures are not very exact. In Mo_9O_{26} the Mo—O distances vary between 1.8 and 2.1 Å with an average value of 1.91 Å and the O—O distances between 2.5 and 3.0 Å. For Mo_8O_{23} the limits of the Mo—O distances are 1.8 and 2.2 Å with an average value of 1.94 Å while the O—O distances fall within 2.5—2.9 Å. In both oxides the lengths of O—O edges common to two MoO_6 octahedra are $\sim$ 2.5 Å.

The idealized structures, obtained by joining boards of regular octahedra in a manner corresponding to the way in which the two oxides are built up, are illustrated in Fig. 7, showing projections parallel to the direction of the infinite extension of the boards. The axial ratios of the actual structures based on 3.75 Å as unit length — which may be a probable value of the length of the space diagonal of a regular MoO_6 octahedron — are in harmony with the values calculated for the idealized lattices, apart from the *b* axes being extended. The agreement between idealized and actual values of the monoclinic angles is also good.

		$a:b:c$	β
Mo_9O_{26}	Idealized lattice	4.48 : 1 : 3.82	93°4
	Actual lattice	4.47 : 1.07 : 3.85	96°
Mo_8O_{23}	Idealized lattice	4.48 : 1 : 3.53	108°4
	Actual lattice	4.48 : 1.08 : 3.57	106°5

SUMMARY

Two molybdenum oxides of compositions close to $MoO_{2.90}$ (β' and β oxide) have been investigated by means of X-rays. Their formulae have been shown to be Mo_9O_{26} and Mo_8O_{23}. Complete determinations of the structure have been carried out, showing pronounced similarity between the two structures. Both oxides are built up of MoO_6 octahedra coupled together by sharing corners or edges. Formally, two-dimensional layers of MoO_6 octahedra joined by corners may be looked upon as larger elements of the lattices. These »boards» are of infinite length in one direction but of finite, characteristic extension in the other, *viz.* 9 octahedra for Mo_9O_{26} and 8 for Mo_8O_{23}.

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