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On the Crystal Structure of Molybdenum Trioxide

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In 1931 two papers on the crystal structure of molybdenum trioxide appeared in the *Zeitschrift für Kristallographie* reporting the work on this subject carried out independently by Braekken[1] and N. Wooster[2]. The results obtained by these authors agree fairly well and there has been no reason to question the principal features of the structure as given by them. The structure has also been confirmed by the present investigation. Molybdenum trioxide thus crystallizes with four formula units of MoO_3 in the orthorhombic elementary cell and with the symmetry *Pbnm*. The molybdenum atoms coordinate six oxygen atoms to form MoO_6 octahedra, which are joined by sharing edges to form zigzag shaped rows. The rows are mutually connected by corners to layers, which are placed on top of each other without having atoms in common. Three of the six oxygen atoms surrounding every molybdenum atom are thus common to three MoO_6 octahedra, two of them belonging to two octahedra and the sixth one being unshared.

In connection with crystal structure investigations of a number of molybdenum oxides carried out at this Institute in recent years, it has been thought desirable to determine the interatomic distances for molybdenum trioxide with a higher degree of accuracy than was obtained in those early investigations in which the oxygen positions were settled from considerations of space only.

X-RAY DATA

Accurate unit cell dimensions of molybdenum trioxide have been calculated by Hägg and one of the present authors[3] from X-ray powder photographs obtained with focusing cameras and Cr-*K* radiation from a preparation (Kahlbaum *puriss.*) that had been heated for 15 hours at 200° C. The figures obtained in this way are in excellent agreement with those given by Braekken. *Cf.* Table 1.

*Table 1. Unit cell dimensions *.*

Authors	a Å	b Å	c Å	V Å^3
Braekken [1]	3.962	13.855	3.701	203.1
Wooster [2]	3.93	13.97	3.67	201
Hägg and Magnéli [3]	3.966	13.85	3.696	203.0

* The figures for the lengths of the axes given in the various papers are here multiplied by 1.002 in order to bring the dimensions on the true Å unit basis [4].

A needle-shaped crystal out of a sample obtained by sublimating the Kahlbaum preparation mentioned above was used for the single-crystal investigation. Mo-K radiation was used in order to get a large number of reflections and to minimize the influence of absorption. Due to the crystals being extremely thin it was only possible to obtain photographs with rotation around the needle axis. In this way Weissenberg photographs were registered for the layer lines 0—4. Multiple film technique was applied [5]. In order to bring about appropriate decrease of the blackening of the spots within subsequent photographs of the pack thin iron foils (about 20 μ) were inserted between the sheets of film.

Relative intensities of the reflections were estimated visually by comparison with an intensity scale obtained by exposing an interval of the zero layer line of the crystal with different exposure times on one pack of films. Correlation between the various layer lines was procured by means of a "Weissenberg oscillation photograph" as has been described elsewhere [6].

The structure amplitudes were computed by multiplying the intensity values by $\cos^2 \mu \cdot \sin \Upsilon/(1 + \cos^2 2\Theta)$ utilizing the curves given by Lu [7]. The temperature factor was neglected.

DETERMINATION OF THE ATOMIC PARAMETERS

According to the unanimous statements of Braekken and Wooster all the atoms of molybdenum trioxide are situated in the symmetry planes of the centrosymmetrical space-group *Pbnm* occupying fourfold point positions 4(c)*:

$$x\ y\ \tfrac{1}{4};\tfrac{1}{2}-x,\ \tfrac{1}{2}+y,\tfrac{1}{4}\ ;\ \tfrac{1}{2}+x,\ \tfrac{1}{2}-y,\ \tfrac{3}{4};\ \overline{x}\ \overline{y}\ \tfrac{3}{4}.$$

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* Notations analogous to those of space-group D_{2h}^{16}-*Pnma* in *International tables for the determination of crystal structures,* Berlin (1935).

All the atomic parameters may thus be determined by investigating the section ϱ (x y $\frac{1}{4}$) of the three-dimensional electron density function.

On the basis of the parameter values given by Wooster it was possible to derive the signs of the structure factors of most reflections h k l. The section mentioned above could thus be preliminarily calculated *. Within the considered area ($0 \leq x \leq 60/60$, $0 \leq y \leq 60/120$) the resulting map showed one heavy maximum and three minor ones in approximate agreement with the positions assumed for the molybdenum and oxygen atoms. The atomic coordinates obtained in this way permitted a calculation of the signs of almost all of the registered structure factors. The section ϱ (x y $\frac{1}{4}$) derived on the basis of the entire number of observed reflections gave the parameter values listed in Table 2. The structure factor values corresponding to these atomic positions are in fair agreement with the observed ones.

Table 2. Atomic parameters.

	Parameter values according to					
	Braekken [1]		Wooster [2]		the present investigation *	
	x	y	x	y	x	y
4Mo in 4(c)	0.088	0.101	0.086	0.0985	0.0847	0.0998
4O_1 in 4(c)	0.588	0.43	0.586	0.4305	0.525	0.435
4O_2 in 4(c)	0.588	0.101	0.586	0.0985	0.56	0.100
4O_3 in 4(c)	0.088	0.250	0.086	0.250	0.015	0.230

* The molybdenum coordinates are very exact. The error in x is probably about ± 0.001 and the accuracy in y is even greater. The oxygen positions may be correct within about one per cent.

DISCUSSION

As is clear from Table 2 the molybdenum parameters obtained in this investigation are in close accordance with those derived by the previous authors. Concerning the oxygen atoms, however, there are certain considerable changes of the coordinates, *viz.* for the oxygen atoms denoted O_1 and O_3. Interatomic distances calculated on the basis of the new parameter values are listed in Table 3 (*cf.* Fig. 1). They are throughout of plausible lengths. The

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* The Fourier summations were facilitated by using the Hägg-Laurent calculating machine [8] and the Robertson strips [9].

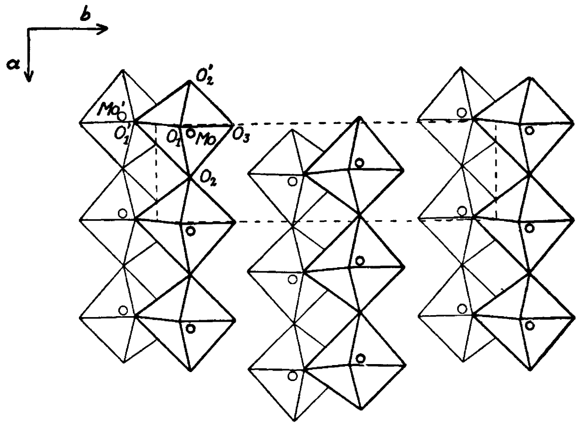

Fig. 1. Molybdenum trioxide viewed along [001]. Molybdenum atoms (small rings) at $z = \frac{3}{4}$ *and the surrounding octahedra are indicated by heavy lines, those at* $z = \frac{1}{4}$ *by thin lines. The extension of one unit cell is indicated by dashed lines. N. B. The oxygen atom* O_1 *is not identical with the one similarly denominated in Table 2, but related to the latter through a glide plane n normal to [010].*

Table 3. Interatomic distances (cf. Fig. 1).

Mo—Mo'	3.43 Å	$O_1 - O_1'$	2.6 Å
Mo—Mo (‖ [100])	3.97	$O_1 - O_2$	2.85
Mo—Mo (‖ [001])	3.70	$O_1 - O_3$	3.05
		$O_1 - O_2'$	2.65
$Mo - O_1$	2.05	$O_1' - O_2$	3.25
$Mo - O_1'$	2.35	$O_2 - O_3$	2.8
$Mo - O_2$	1.85	$O_3 - O_2'$	2.6
$Mo - O_2'$	2.1	$O_2' - O_1'$	2.85
$Mo - O_3$	1.8		

displacement of O_1 involves a decrease to 2.6 Å of the distance O_1—O_1' as compared with the value of about 2.75 Å calculated from the data of Braekken and Wooster. It seems quite reasonable that this edge, being shared by two MoO_6 octahedra, is relatively short. The shift in the position of O_3 makes the distance Mo—O_3 the shortest one within the octahedron. This also seems natural as the O_3 atom contrary to the other oxygen atoms is in contact with one metal atom only.

In a recent paper from this Institute[10], interatomic distances have been listed for molybdenum oxides and related compounds previously investigated by one of the present authors. For molybdenum trioxide the distance of 3.70 Å between the metal atoms of octahedra joined by sharing corners and belonging to the same row is in agreement with the normal value observed for a great number of molybdenum and tungsten compounds. The distance between molybdenum atoms of connected rows is considerably longer (3.97 Å) and approaches the figure observed for the distances between the puckered sheets of metal atoms in Mo_8O_{23} and Mo_9O_{26}. The distance for octahedra joined by edges (3.43 Å) exceeds the values observed for other molybdenum oxides. This is probably due to the repulsion between adjacent molybdenum atoms not being counter-balanced by further metal atoms in the trioxide.

The considerable variations of the molybdenum-oxygen and oxygen-oxygen distances of molybdenum trioxide evidently also depend on the layer character of the lattice.

SUMMARY

An investigation of the crystal structure of molybdenum trioxide by means of Fourier methods has confirmed the principal features of the structure reported by Braekken and N. Wooster, and given accurate atomic positions. The interatomic distances are compared with those previously obtained for other molybdenum oxides and related compounds.

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