On the Existence of a Metallic Molybdenum Oxide

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Studies of the molybdenum oxides carried out by Magnéli have revealed the existence of three phases, Mo_4O_{11} ¹, Mo_8O_{23} ² and Mo_9O_{26} ², besides MoO_2 and MoO_3 .

The present investigation was started in order to look for the existence of molybdenum oxides with low oxygen content. Finely powdered molybdenum metal (Lindbergh, 99.6 %) was carefully oxidized in different ways. The following method caused the formation of an oxide phase, not described in the literature. MoO_2 , obtained by reduction of MoO_3 (Kahlbaum, *puriss.*) with hydrogen, and Mo powder were mixed in proportions corresponding to the gross compositions $\text{MoO}_{0.25}$, $\text{MoO}_{0.50}$, $\text{MoO}_{0.75}$, $\text{MoO}_{1.00}$. The samples were packed in small alumina tubes, placed in silica tubes, which were then evacuated, sealed and heated at 1 000°C after which the temperature was lowered to 400°C at a constant rate of 10°C per day.

The phase analysis of the specimens was performed by means of powder photographs taken in focussing cameras of the Guinier type using $\text{CuK}\alpha$ radiation. For measurement of the high-angle reflections additional photographs were taken in Hägg-Phragmén focussing cameras.

Besides the diffraction patterns of Mo and MoO_2 the photographs contained the lines of a face-centered cubic phase with the axial length $a = 5.549 \text{ \AA}$ ($V = 170.9 \text{ \AA}^3$). It was not possible to prepare the new oxide in a pure state. The samples of the compositions $\text{MoO}_{0.25}$ and $\text{MoO}_{0.50}$ only contained small amounts of Mo and MoO_2 , however. The amount of MoO_2 was considerably greater for the composition $\text{MoO}_{0.75}$ and $\text{MoO}_{1.00}$, indicating a probable oxygen content of between 20 and 30 atom-% for the metallic oxide. The formula is formally given here as Mo_3O , although the oxygen content may differ to some extent from 25 atom-%.

As only reflections with $h + k = 2n$, $k + l = 2n$, $h + l = 2n$ appeared in the photographs, the atoms have a face-centered arrangement. Space is available for the metal atoms only in the following positions: $(0,0,0)$; $0, \frac{1}{2}, \frac{1}{2}$; $\frac{1}{2}, 0, \frac{1}{2}$; $\frac{1}{2}, \frac{1}{2}, 0$ + 4 (a) $0,0,0$; 4 (b) $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$; 4 (c) $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$; 4 (d) $\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$. The reflections with $h + k + l = 4n$ are considerably stronger than those with $h + k + l \neq 4n$. From the $|F|^2$ values calculated for different combinations of atomic positions it is evident (Table 1) that the metal atoms are situated in 4 (a) $0,0,0$ + 4 (c) $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ + 4 (d) $\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$.

Table 1. Intensities calculated and observed for the Mo_3O phase.

<i>hkl</i>	<i>I</i> _{calc.}	<i>I</i> _{obs.}
1,1,1	13	15
2,0,0	7	10
2,2,0	44	45
3,1,1	7	10
2,2,2	2	2
4,0,0	12	10
3,3,1	5	5
4,2,0	4	5
4,2,2	28	25
3,3,3	1)	3
5,1,1	3)	
4,4,0	11	10
5,3,1	5	5
4,4,2	2)	2
6,0,0	1)	
6,2,0	19	15
5,3,3	2	2
6,2,2	2	2
4,4,4	11	10

For pure Mo the measured value of the lattice constant was $a = 3.126 \text{ \AA}$ meaning a volume per metal atom of $15.28 \text{ \AA}^3$. The corresponding volume is obtained for a cell content of 11.2 Mo atoms in the oxide phase. As the presence of oxygen (20–30 atom-%) most likely causes an expansion, the unit cell cannot contain more than 11 Mo atoms. The density observed for the Mo_3O samples was 8.6. As they contained small amounts of Mo and MoO_2 this value is not reliable but indicates a cell content of approximately 3 formula units Mo_3O . The density calculated for this case will be 8.86.

With the above presumptions the configuration of Mo_3O is 3 Mo in 4 (*a*) 0,0,0 and 6 Mo in 8 (*c*) $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ in the space-group $O_h^5\text{-}Fm\bar{3}m$. The atoms are distributed at random over these positions. A Mo atom in 8 (*c*) is surrounded by 3 Mo atoms in 4 (*a*) and 6 Mo atoms in 8 (*c*) at the distances of 2.40 Å and 2.77 Å respectively giving a mean value of 2.65 Å. A Mo atom in 4 (*a*) is surrounded by 6 Mo atoms in 8 (*c*) at a distance of 2.40 Å, which value is remarkably small as compared with the interatomic distances in the pure metal, 2.71 Å. The discrepancy is partially due to the lowering of the coordination number from 8 to 6 and may also be partially due to the degree of Mo-O ionisation.

The oxygen atoms (approximately three atoms) can be situated in the remaining 4 (*a*) and 8 (*c*) positions or the 4 (*b*) $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ positions of the space-group $Fm\bar{3}m$. As the observed O—O distances, even in oxides with metallic character, have always been found to exceed the value of 2.5 Å the former grouping is excluded. The Mo—O distances, with the oxygen atoms in 4 (*b*), are as great as the Mo—Mo distances — close to the radius sum $r_{\text{Mo}} + r_{\text{O}^{2-}} = 1.35 \text{ \AA} + 1.32 \text{ \AA} = 2.67 \text{ \AA}$. The corresponding abnormally great metal-oxygen distances have been observed for the metallic oxides Cr_3O^3 and W_3O^4 of the “ordered” and “disordered” A 15 type respectively. This cannot with the

greatest probability be a contingency in all three cases, but can be explained by an electron displacement from the metal atoms — at most $2/3$ electrons per metal atom — to the oxygen atoms. The decrease of the radius value of the metal atom will therefore be very small, and there are still “free” electrons available in the outer s and d shells for the formation of metal-metal bonds.

The atomic arrangements of the three metallic oxides in group VI a (Cr_3O , Mo_3O , W_3O) form intermediate stages between the cubic close-packing (A 1) and the cubic body-centered lattice (A 2).

Attempts to prepare Mo_3O by oxidation of Mo powder at temperatures between 600°C and 800°C by means of steam in the presence of hydrogen in excess failed owing to the ease with which MoO_3 and MoO_2 forms. Oxidation of Mo by means of Cu_2O in evacuated and sealed silica tubes at 650°C for two weeks only caused the formation of small amounts of Mo_3O . No trace of the oxide was obtained in Mo- MoO_2 samples heated in vacuum furnaces at various temperatures between 1100°C and 1600°C . It may be, therefore, that Mo_3O is unstable at these high temperatures.

SUMMARY

A metallic molybdenum oxide with the probable ideal formula Mo_3O has been prepared by the reaction between Mo powder and MoO_2 at a comparatively low temperature. The structure of the oxide is related to that of the Cr_3O and W_3O phases of the “ordered” and “disordered” A 15 type respectively.

9 Mo atoms are distributed at random over the positions 4 (a) $0,0,0$ + 8 (c) $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ in the space-group $O_h^5\text{-}Fm3m$ and the O atoms are most likely located in the position 4 (b) $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ implying a crystal lattice of a defective BiF_3 type.

The magnitude of the Mo—O distances seems to indicate a fairly large ionisation of the O atoms.

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