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On the MoO_2 Structure Type

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The crystal structure of vanadium dioxide may be considered as representing the idealized form of the MoO_2 structure type, which also comprises dioxides of molybdenum, wolfram, technetium, and rhenium. The structure is of a deformed rutile type, the metal atoms occurring in doublets. The bond distances are correlated to the number of valence electrons of the metal atoms.

The crystal structures of the isomorphous dioxides of molybdenum and wolfram may be described as being of a deformed rutile type [1]. Thus the metal atoms coordinate six oxygen atoms to form MeO_6 octahedra which are joined by sharing edges to form strings. The strings are mutually connected to a threedimensional structure by octahedra having corners in common. In the ideal rutile structure type, the metal atoms are equidistantly arranged within the strings. In the MoO_2 structure type, however, the metal atoms are alternately nearer to and farther from each other. This results in a pronounced formation of metal atom doublets and distortion of the MeO_6 octahedra. The symmetry is also correspondingly lowered from tetragonal for the rutile type to monoclinic for the MoO_2 structure type. The structures are illustrated in Fig. 1.

The symmetry actually derived for molybdenum and wolfram dioxide is $P2_1$ (No. 4). However, for both compounds only a few weak reflexions $h0l$ (h odd) were observed, which indicates that the symmetry is very close to $P2_1/a$ (No. 14). If the orientation $P2_1/c$ is chosen in order to bring about conformity with the usual notation given in the International Tables for X-Ray Crystallography, the atomic arrangement of molybdenum dioxide is very nearly given by the following table, which is in accordance with the previously published data within the accuracy of the structure determination [1].

MoO_2: Space-group: $P2_1/c$

4 Mo in 4(*e*):	$xyz;\ \bar{x}\bar{y}\bar{z};\ \bar{x},\ \frac{1}{2}+y,\ \frac{1}{2}-z;\ x,\ \frac{1}{2}-y,\ \frac{1}{2}+z$
	$x = 0.232,\ y = 0.000,\ z = 0.017$
4 O_I in 4(*e*):	$x = 0.11,\ y = 0.21,\ z = 0.24$
4 O_{II} in 4(*e*):	$x = 0.39,\ y = 0.70,\ z = 0.30.$

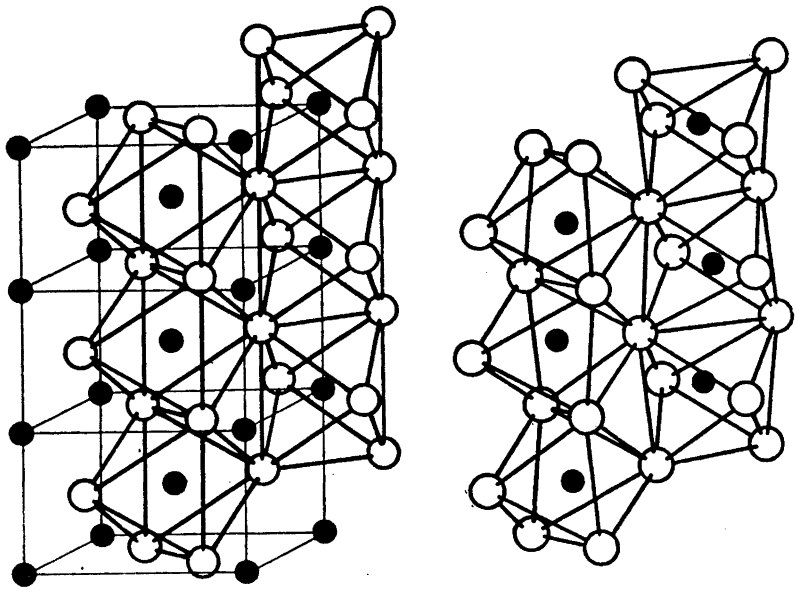

Fig. 1. a) The rutile structure type. MeO_6 octahedra are joined by sharing edges to form strings, which are mutually connected by corners. Three unit cells are indicated.

b) The MoO_2 structure type. The MeO_6 octahedra are joined in the same way as in rutile but the Me atoms within the strings are pairwise drawn nearer to each other to form doublets, which causes distortion of the octahedra.

For titanium dioxide (rutile) an analogous description would give the following set of atomic positions [2,3]:

TiO_2: Space-group: $P2_1/c$

4 Ti in 4(*e*): $x = 0.250$, $y = 0.000$, $z = 0.000$
4 O_I in 4(*e*): $x = 0.097$, $y = 0.194$, $z = 0.194$
4 O_{II} in 4(*e*): $x = 0.403$, $y = 0.694$, $z = 0.306$.

The occurrence of metal atom doublets in the MoO_2 structure type is of considerable interest and the findings of Zachariasen [4] that there exist dioxides of technetium and rhenium belonging to this type adds to the importance of this structural feature. However, the latter compounds could only be prepared in powder form, and the powder photographs were too complicated to allow a determination of the atomic positions to be made [5].

Recently, one of the present authors (G.A.) in the course of studies on the vanadium-oxygen system has performed a complete structure determination for vanadium dioxide [6]. The unit cell dimensions are similar to those of the dioxides of MoO_2-type (*cf.* Table 1) and the atomic arrangement is in close agreement with the idealized structure of molybdenum dioxide given above.

VO_2: Space-group: $P2_1/c$

4 V in 4(*e*): $x = 0.242$, $y = 0.975$, $z = 0.025$
4 O_I in 4(*e*): $x = 0.10$, $y = 0.21$, $z = 0.20$
4 O_{II} in 4(*e*): $x = 0.39$, $y = 0.69$, $z = 0.29$.

No reflexions, indicating a deviation from the symmetry $P2_1/c$, could be observed for vanadium dioxide and it is obvious that this compound may be considered as representing the idealized form of the "MoO_2 structure type".

The occurrence of metal atom doublets in molybdenum and wolfram dioxide has been discussed by Pauling [9], who suggests that each of the quadrivalent metal atoms has a tendency to use its two remaining valence electrons for the formation of a double bond with another metal atom. The influence of the number of valence electrons on the bond length within the doublets is illustrated in Table 2. The data given for technetium and rhenium dioxide are calculated assuming the metal atom positions of these compounds to be equal to those of molybdenum dioxide, which assumption seems to be justified by the close similarity of the lattice dimensions. The longer metal-metal atom distances within the strings of MeO_6 octahedra are very nearly the same for the various dioxides of the MoO_2 structure type but considerably longer than the corresponding distance in the titanium dioxide (rutile) structure. A detailed comparison, however, is rendered a little difficult by the fact that the metal

Table 1. Unit cell dimensions of dioxides of the MoO_2 structure type and comparable data for titanium dioxide (rutile). Space-group $P2_1/c$ *(No. 14).*

Compound	*a* Å	*b* Å	*c* Å	*β*	Reference
TiO_2(rutile)	5.918	4.593	5.464	122°79	2
VO_2	5.743	4.517	5.375	122°61	7
MoO_2	5.584	4.842	5.608	120°94	8
WO_2	5.565	4.892	5.650	120°69	8
TcO_2	~5.53	~4.79	~5.53	~120°	4
ReO_2	5.562	4.838	5.561	120°87	5

Table 2. Some interatomic distances of dioxides of the MoO_2 structure type and of titanium dioxide (rutile).

Compound	Number of valence electrons of metal	Me-Me distances within strings of MeO_6 octahedra	O-O distance along edge common to two MeO_6 octahedra of Me atom doublet	Reference
TiO_2 (rutile)	4 + 0	2.959	2.520	2, 3
VO_2	4 + 1	2.65; 3.12	2.62	6
MoO_2	4 + 2	2.50; 3.10	3.1	1, 8
WO_2	4 + 2	2.49; 3.08		1, 8
TcO_2	4 + 3	(2.48); (3.06)		4
ReO_2	4 + 3	(2.49); (3.08)		5

atoms considered belong to different periods of the periodic system. With decreasing bond distance within the metal atom doublets, the distance between the oxygen atoms of the edge common to the two MeO_6 octahedra is markedly increased.

It might be possible to obtain further knowledge of the bond conditions of compounds of this type by studying mixed oxides, *e. g.* of the system titanium dioxide-vanadium dioxide. Such experiments will be started in the near future. A detailed account of the determination of the structure of vanadium dioxide will shortly appear elsewhere.

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