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A Crystallographic Examination of Tungsten Trioxide Whiskers

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Fine, whisker-like crystals containing W, Mo, and oxygen and free from other metals, grown from the vapour phase, are related in structure to the hexagonal form of tungsten bronze. Two different phases have been found, the evidence suggesting that they are structural homologues $MoW_{3n-1}O_{9n}$ ($n=4, 5$), the Mo replacing some of the W in certain crystallographic sites, and with no impurity atoms in the twelve-coordinated interstitial positions.

Tungsten trioxide exists in several polymorphic varieties which are reversibly formed by heating or cooling to well defined temperatures (Wyart & Foëx, 1951; Matthias & Wood, 1951). Some of these are known to be related to the simple cubic structure for which ReO_3 serves as the model, but atomic displacements, introduced in various ways, cause symmetry differences (Andersson, 1953; Kehl, Hay & Wahl, 1952).

In the present study tungsten trioxide, formed from the vapour phase, was found to have diffraction data unrelated to any of these. Whilst it has been difficult to establish the exact formula, the crystallographic evidence suggests that at least two stoichiometric compounds can be identified in which small amounts of molybdenum play a vital role.

Experimental

Commercial tungsten trioxide, containing 0·1% MoO_3 as impurity, was heated in an electric furnace to 1200 °C. A fuzz of extremely thin colorless crystals grew rapidly on the alumina crucibles used as loose plugs in the ends of the furnace tube. Prolonged heating failed to increase the yield, and at no time have more than a few micrograms of material been available for study. Qualitative analysis by X-ray spectroscopy* showed a considerable enrichment of molybdenum, but no other kinds of element identifiable by this means were present in any quantity.

A powder photograph taken on a Guinier-type focusing camera could be partly indexed as hexagonal with the lattice parameters $a=7·29$, $c=3·834$ Å, but several weak and diffuse lines were also present which could not be assigned indices.

Several whiskers, each a few tenths of a millimetre in length, were mounted, and two of them gave good diffraction patterns. The first of these could be indexed as orthorhombic with

$$a=7·29,\ b=25·26,\ c=3·834\ \text{Å}$$

and with no systematically absent reflexions. This limited the space group to *P*222, *Pmm*2 or *Pmmm*. The presence of extremely weak and diffuse streaks which would require a and c to be doubled suggested that some stacking disorder was present.

A feature of these data was the strong hexagonal pseudo-symmetry already referred to. The unit cell which was chosen was, in fact, the orthohexagonal one, but with the b dimension doubled.

The $hk0$ intensities were recorded with the multiple-film technique using filtered copper radiation, and the measurements, after suitable corrections, were subsequently placed on an absolute scale by comparison with the calculated structure factors. These were derived from the scattering curves for tungsten and molybdenum by Thomas & Umeda (1957) and for oxygen by Viervoll & Øgrim (1949).

This crystal was unfortunately lost before additional intensity information was recorded, and another of the same diffraction characteristics could not be found. This restricted the scope of the present study.

The other crystal, a twin, showed the same pseudo-symmetry, but was centred on (001) with

$$a=7·29,\ b=63·1,\ c=3·834\ \text{Å}\ .$$

In this case b was five times the orthohexagonal b axis.

It became clear, therefore, that differences existed between one crystal and another from this single preparation, and whilst the structures of these two were basically the same, the different superlattices could be assumed to reflect differences either of chemical composition or of stacking in the structural units. With such a minute amount of material, only a limited description, relying solely upon X-ray methods, could be made.

Derivation of the structure of $MoW_{11}O_{36}$

The dimensions of the sub-cell were strikingly similar to those of the intensely colored hexagonal tungsten bronzes, the structure of which was deduced by Magnéli (1953). The $hk0$ structure factors for the sub-

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* By courtesy of Mr P. R. Brett, P.M.G. Research Labs., Melbourne.

cell were computed on the assumption that the metal atoms were all of equal scattering power, and at the ideal lattice positions of the bronze; there was remarkably good agreement with the observed data. The reliability quotient was 17·5% assuming a temperature factor $B=0{\cdot}3$ Å^2. The structure of the tungsten-trioxide whiskers was therefore related to the bronze, and the problem resolved itself into finding the cause of the different forms of the superlattice.

The extra reflexions could be due to movements of metal atoms, or of oxygens, from the ideal positions assumed for them. Trial-and-error calculations in which tungsten was moved so as to give unit cells of the two kinds showed that the effect at low angles was too small, and at high angles too large, to be seriously considered. A difference Patterson function was prepared in which the calculated contributions of the metal atoms, all assumed to be tungsten, weighted with a temperature factor $B=0{\cdot}3$ Å^2 and suitably scaled, were subtracted from the $F_o^2(hk0)$ terms. This is shown in Fig. 1(*b*) together with a sketch of the metal positions which had been assumed (Fig. 1(*a*)). The metal-to-metal vectors sites form three groups; *A*, *B* and *C* are positive, *D* and *E* are almost zero, and *F* and *G* are negative. The metal atoms 1, 2, 3 and 4 in Fig. 1(*a*) all contribute to *D*, *E*, *F* and *G* but not to *A*, *B* and *C*. Eight metal atoms contribute to *A*, *B* and *C*, eight to *F* and *G*, and twelve to *D* and *E*. Clearly, therefore, one or all of the atoms 1–4 has a lower atomic number than the remainder. The residual peaks of the Patterson function, due in part to W–O interactions, are considerably extended, and the octahedral oxygen grouping around each tungsten is evidently distorted.

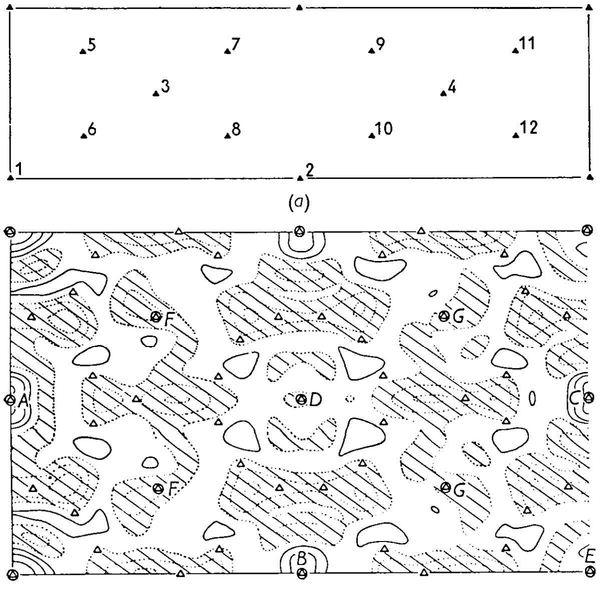


Fig. 1. (*a*) Ideal tungsten arrangement. (*b*) The difference Patterson function projected on (001). This was prepared by removing the vectors due to the ideal arrangement of Fig. 1(*a*). Negative areas are shaded; open triangles refer to ideal W–O vectors, and circles to W–W vector sites.

Fig. 1(*b*) is not consistent with an explanation of the superlattice based upon the presence of scattering material in certain of the twelve co-ordinated interstitial positions. In the tungsten bronze itself these are occupied by the alkali metal ions K, Rb, or Cs, which, by creating valancy anomalies in the tungsten lattice, are primarily responsible for the metallic characteristics for which the trivial name 'bronze' is given. Our crystals are all colorless. A Fourier projection $\varrho(x, y)$ in which only the sub-cell terms were included, whilst not reflecting the true symmetry of the larger super-lattice, gave no evidence of matter in the interstitial positions, but confirmed that sites 1–4 contained material of substantially lower scattering power than the remainder: the higher symmetry, however, prevented a choice between them.

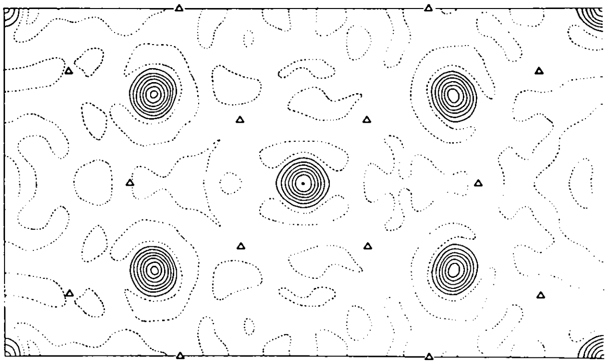


Fig. 2. The $F(hk0)$ Fourier summation for $MoW_{11}O_{36}$. Signs were assumed to be unaffected by oxygens. Open triangles are ideal oxygen positions.

It was concluded that Mo^{6+} atoms, found spectroscopically, may replace some, or all, of the tungsten atoms 1–4. Trial-and-error calculations showed that the diffraction data were best satisfied by placing only one Mo in the unit cell, and this could arbitrarily be at the origin.

An *hk*0 Fourier projection, based on this argument and assuming the space group *Pmmm* is shown in Fig. 2. The peaks are of good shape, are shifted little, if at all, from the ideal positions, and the heights are self-consistent. The observed and calculated values of $F(hk0)$ are given in Table 1, and in these, only the scattering from the metal atoms in the positions listed in Table 2 is included. The temperature factor is $B=0{\cdot}34$ Å^2. The reliability factor for the pseudo-hexagonal reflexions is now 14%, but the agreement with the superlattice reflexions is poor.

It appeared, therefore, that the assumptions were essentially correct, but it remained to account for the variations of intensity in the intermediate reflexions. An $F_{\text{obs.}} - F_{\text{met.}}$ synthesis was computed. This revealed *pairs* of poorly resolved peaks in the neighbourhood of the ideal oxygen positions, and if these are real,

Table 1. $MoW_{11}O_{36}$. *Comparison of F_o with F_c (metal atoms alone)*

*hk*0	F_o	F_c
0*k*0		
1	67	−32
2	50	−32
3	70	−32
4*	287	−297
5	<47	−31
6	84	−30
7	89	−30
8*	633	713
9	<48	−28
10	<52	−28
11	110	−27
12*	277	−246
13	<61	−25
14	111	−24
15	<68	−23
16*	544	549
17	<74	−22
18	<77	−21
19	<80	−20
20*	142	−181
21	<85	−19
22	<86	−18
23	<87	−17
24*	422	391
25	<85	−16
26	<83	−15
27	<79	−15
28*	149	−128
29	<69	−14
30	<62	−13
31	<53	−12
32*	229	271
1*k*0		
0	61	−31
1	58	−31
2*	245	235
3	72	−31
4	75	−31
5	82	−30
6*	229	223
7	43	−29
8	67	−29
9	<50	−28
10*	124	204
11	<56	−26
12	58	−25
13	<63	−25
14*	208	179
15	<69	−23
16	<72	−22
17	<76	−22
18*	111	153
19	<81	−20
20	<84	−19
21	<85	−18
22*	122	129
23	<87	−17
24	<86	−16
25	<85	−16
26*	116	108
2*k*0		
0*	313	−283
1	77	−30
2	72	−30
3	67	−30
4*	713	713
5	<47	−29
6	<52	−28
7	72	−28
8*	192	−258
9	97	−26
10	116	−26
11	<61	−25
12*	538	595
13	<67	−23
14	<70	−23
15	<72	−22
16*	213	201
17	<79	−21
18	114	−20
19	<84	−19
20*	491	444
21	<87	−18
22	<87	−17
23	<87	−17
24*	148	−146
25	<83	−15
26	<79	−15
27	<75	−14
28*	294	314
3*k*0		
0	75	−27
1	91	−27
2*	119	204
3	<54	−27
4	77	−27
5	<56	−26
6*	248	194
7	84	−25
8	61	−25
9	89	−24
10*	197	179
11	67	−23
12	<71	−23
13	<73	−22
14*	141	162
15	<78	−21
16	<80	−20
17	<83	−19
18*	119	138
19	<86	−18
20	<87	−18
21	<87	−17
22*	<86	117
23	<84	−16
24	<82	−15
25	<79	−15
26*	104	100
4*k*0		
0*	462	595
1	<64	−24
2	64	−24
3	<65	−24
4*	279	−225
5	67	−23
6	97	−23
7	<69	−23
8*	562	549
9	<72	−22
10	<74	−22
11	77	−21
12*	227	−194
13	<80	−20
14	82	−20
15	<84	−19
16*	429	444
17	<86	−18
18	<87	−18
19	<87	−17
20*	149	−150
21	<85	−16
22	<83	−15
23	<80	−15
24*	312	329
5*k*0		
0	75	−21
1	106	−21
2*	169	162
3	108	−21
4	133	−21
5	134	−21
6*	156	153
7	<79	−20
8	<80	−20
9	<82	−20
10*	82	143
11	<84	−19
12	<85	−19
13	<86	−18
14*	182	130
6*k*0		
0*	179	−175
1	146	−19
2	119	−19
3	84	−19
4*	491	444
5	<85	−18
6	<86	−18
7	<86	−18
8*	182	−169
9	<87	−18
10	<87	−17
11	<87	−17
12*	356	391
13	<86	−16
14	<85	−16
15	<84	−16
16*	116	−139
17	<80	−15
18	<77	−14
19	<74	−14
20*	277	314
7*k*0		
0	86	−16
1	<86	−16
2*	149	117
3	<86	−16
4	<86	−16
5	<85	−16
6*	170	114
7	<85	−16
8	<84	−16
9	<83	−15
10*	173	108
8*k*0		
0*	213	329
1	<76	−14
2	<76	−14
3	<75	−14
4*	<74	−128
5	<74	−14
6	<72	−14
7	<71	−14
8*	195	314

* Sub-cell reflexions marked with asterisk.

Table 2. *Fractional atomic parameters for metal atoms in* $MoW_{11}O_{36}$

Space group assumed to be *Pmmm*

	Pt. posn.	*x*	*y*	*z*
Mo	1(*a*)	0	0	0
W	1(*e*)	0	½	0
W	2(*o*)	½	¼	0
W	4(*y*)	¼	⅛	0
W	4(*y*)	¼	⅜	0

the unit cell must include at least two octahedral layers, in which the oxygen atoms alone are in slightly different positions. This would account for the poorly resolved intermediate 00*l* layer lines.

Table 3. *y Parameters for oxygen used to compute Table* 4

Atom	Multiplicity	Ideal	Distorted
01	1	0	0
02	1	0·500	0·500
03	2	0·106	0·106
04	2	0·144	0·144
05	2	0·250	0·240
06	2	0·356	0·356
07	2	0·394	0·394
08	4	0·053	0·063
09	4	0·125	0·110
010	4	0·197	0·212
011	4	0·303	0·313
012	4	0·375	0·390
013	4	0·447	0·462

Table 4. *Calculated and observed* (0*k*0) *structure factors including oxygen*

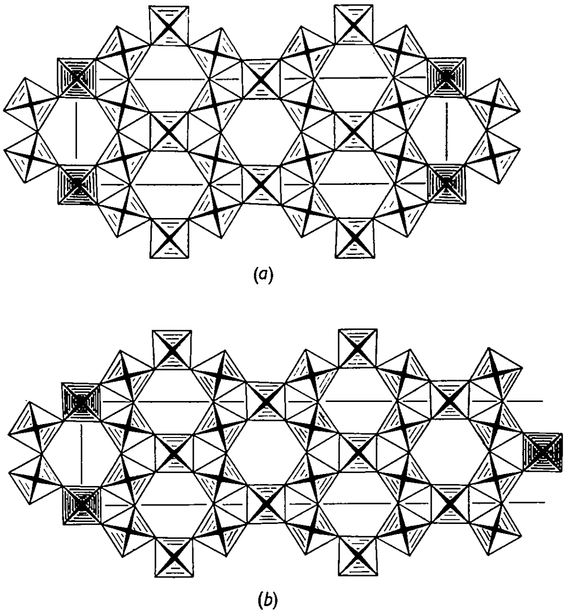
0*k*0	F_o	F_c	0*k*0	F_o	F_c	0*k*0	F_o	F_c	0*k*0	F_o	F_c
010	67	−31	090	<48	+13	0,17,0	<74	−10	0,25,0	<85	−25
020	50	+13	0,10,0	<52	+25	0,18,0	<77	+33	0,26,0	<83	+25
030	70	−31	0,11,0	110	−55	0,19,0	<80	−11	0,27,0	<79	−32
040	287	−302	0,12,0	277	−258	0,20,0	142	−163	0,28,0	149	−110
050	47	−31	0,13,0	<61	+13	0,21,0	<85	−32	0,29,0	<69	−5
060	84	−63	0,14,0	111	−75	0,22,0	<86	−65	0,30,0	<62	−52
070	89	−64	0,15,0	<68	+4	0,23,0	<87	−21	0,31,0	<53	−19
080	633	642	0,16,0	544	+517	0,24,0	422	+384	0,32,0	229	+308

The oxygens are not at all well defined, and as there are thirteen independent sets in the unit cell, all of which may have adjustable parameters, the problem of assigning parameters to them is a very formidable one indeed. Under these circumstances it was decided not to refine further, but to show that it was, in fact, possible to obtain better agreement by including oxygen in the structure factors calculated for the 0*k*0 reflexions. The *y* parameters for oxygen, listed in Table 3, were chosen so as to give maximum weight to the 11th and 14th orders and minimum to the 9th and 10th, to be as consistent as possible with the difference synthesis, and at the same time to retain reasonable oxygen-to-oxygen distances within the structure as a whole. These were weighted with an isotropic temperature factor $B = 1{\cdot}0$ Å^2. Table 4 shows a comparison with the observed data which gave a reliability of 15%. Whilst there is no guarantee that the best positions for oxygen have been found, it is nevertheless possible to show that they can influence the intermediate reflexions sufficiently strongly, and it is felt, therefore, that the structure has been solved in principle, if not in detail.

Discussion

The structure is shown in Fig. 3(*a*) where it is drawn as idealized octahedra which are joined by corners to form six-membered rings. These extend out of the plane of the paper to form tunnels running through the length of the crystal. The resulting chemical formula is AX_3. The superlattice is due primarily to the substitution of one molybdenum for every twelfth tungsten, and the unit cell formula is $MoW_{11}O_{36}$.

A second phase with a different unit cell was found, and its probable structure, Fig. 3(*b*), can be inferred by comparison with the first. It will have an ideal formula $MoW_{14}O_{45}$. By comparing these two structures, it seems likely that sites 2, 3, and 4 of $MoW_{11}O_{36}$ could have some Mo substituting isomorphously for W, and this would then provide a mechanism for the transition of one phase to another. A general formula $MoW_{3n-1}O_{9n}$, *n* having values 4 and 5, can now be given. It is tempting, therefore, to suggest that additional phases might be found in which *n* will have other values. If this is so, these members for which *n* is even will have primitive lattices, and those with *n* odd, will have side-centred lattices. Careful studies on the solubility of MoO_3 and WO_3 by solid state reaction (Rieck, 1943; Magnéli, 1949*a*; Westman & Magnéli, 1958) gave no evidence for any of these, and perhaps they can be prepared only from the vapour phase. If this is so, the control of the partial pressures of each component, which would be desirable to form whiskers of only one kind, poses considerable experimental difficulties. If WO_3 whiskers, free of Mo, could be grown then they might be expected to have hexagonal symmetry.


(*a*)

(*b*)

Figs. 3(*a*) and (*b*). The projections of the structures along their *z* axes. The MoO_6 octahedra are fully shaded, and WO_6 octahedra partly shaded. Fig. 3(*a*) is the unit cell of $MoW_{11}O_{36}$, and Fig. 3(*b*) half the unit cell of $MoW_{14}O_{45}$.

The formulation as a series does not imply any relationship to the homologues $(Mo,W)_nO_{3n-1}$ which are so well documented (Hägg & Magnéli, 1954). In this case the two elements Mo and W both appear to be necessary to form the several members, but are statistically distributed over all the metal positions. Furthermore all members are related to the normal form of WO_3, but contain features which can be likened to a mechanism of shear (Wadsley, 1955) in which the *oxygen* content is made to vary by changes of octahedral grouping. One notable omission from this particular series is $W_{18}O_{49}$ which, like our pseudo-hexagonal phases, contains within it empty hexagonal tunnels (Magnéli, 1949*b*). It is interesting to note that this has been identified in needles grown from tungsten metal in an electron-diffraction camera, (Hashimoto, Tanaka, Yoda & Araki, 1958) in which the high vacuum could prevent the formation of an AX_3 type oxide.

We wish to thank Dr L. S. Williams for drawing our attention to the whisker growths.

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The Position of Anomalous Scatterers in Protein Crystals

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A Patterson summation with $\{|F(hkl)|-|F(\bar{h}\bar{k}\bar{l})|\}^2$ coefficients gives peaks at the end of vectors relating the anomalous scatterers in the structure. Application to two mercury derivatives of horse haemoglobin, using Cu $K\alpha$ diffraction data, shows that the ends of vectors between mercury atoms can be recognized easily, and the mercury positions determined, without resorting to isomorphous replacement. Interactions between the iron atoms of the haem groups and the mercury atoms are lost in the background, but can nevertheless be located by removing the spurious background peaks with Buerger's Minimum Function.

Introduction

When a crystal exhibits an observable departure from Friedel's law, in that $F(hkl)$ is markedly different from $F(\bar{h}\bar{k}\bar{l})$, then two types of Patterson functions can be constructed (Okaya *et al.*, 1955; for a summary of this work and general review of the literature see Buerger, 1959, pp. 76–79). The first of these, the cosine function, is defined by

$$P_c(u, v, w)=\frac{1}{V}\sum_h\sum_k\sum_l |F(hkl)|^2 \cos 2\pi(hu+kv+lw)$$

and differs from the normal Patterson only in the detailed shape of the peaks. The second function, defined by

$$P_s(u, v, w)=\frac{1}{V}\sum_h\sum_k\sum_l |F(hkl)|^2 \sin 2\pi(hu+kv+lw)$$

gives positive peaks in one direction and negative peaks in the opposite direction at the end of vectors relating the anomalous scatterers with the remainder of the scattering material in the cell. Neither of these functions has so far been of use in the analysis of protein structures, for the interaction between the anomalous scatterers with the rest of the protein is sufficient to obscure the vectors between the anomalous scatterers themselves.

This paper deals with an attempt to utilize the observed anomalous scattering in order to determine the positions of only those atoms responsible for the deviations from Friedel's law. An application to horse haemoglobin shows that it is possible to determine the position of the heavy mercury atoms from the anomalous data of one compound only, without resorting to any other isomorphous derivative. It was also possible to determine the position of the iron-containing haem groups, without excessive interference from small anomalous scatterers such as sulphur atoms, which are present in fairly large quantities in haemoglobin crystals. This was, therefore, an independent check on the haem positions as found by Perutz *et al.* (1960).