ACTA CHEMICA SCANDINAVICA 7 (1953) 154–158

On the Crystal Structure of Tungsten Trioxide

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An investigation of the structure of tungsten trioxide was carried out in 1931 by Braekken [1], who described the structure as being triclinic (pseudo-monoclinic) having two angles very nearly = 90° and the third showing a slight deviation from this value. He determined the positions of the four tungsten atoms in the unit cell with trial and error methods, and also indicated the probable positions of the twelve oxygen atoms. In fact, this structure corresponds to a monoclinic or orthorhombic symmetry as was also pointed out in the Strukturbericht [2]. However, later reports on this structure vary. When Magnéli [3] interpreted the powder photographs of tungsten trioxide, he did not find any deviation from a monoclinic quadratic form, whereas Wyart and Foëx [4] by measuring single crystals optically came to the conclusion that the symmetry was triclinic. The cell dimensions given by the above mentioned authors are shown in Table 2.

These inconsistencies have made a renewed study of the symmetry of tungsten trioxide desirable. Because work on other tungsten oxides as well as on polytungstates was being carried out in this institute, it also seemed valuable to determine the tungsten positions with Fourier methods.

EXPERIMENTAL

Tungsten trioxide was investigated both with the powder and with the single crystal method. Powder photographs were taken with a Guinier focusing camera using monochromatic Cu-$K\alpha$-radiation. Several preparations of various origins, which had been recrystallized at about 850° C (Merck puriss., Baker analysed, and British Drug Houses) were investigated. They all gave identical powder patterns.

For the single crystal method, minute crystals were obtained from trioxide melts. Rotation and Weissenberg photographs were taken with Cu-K-radiation and with the axes [100] (layer lines 0–4) and [001] (layer lines 0–2) as rotation axes. Multiple film technique was used and the intensities were estimated visually against a scale consisting

of reflections of known relative intensities. The values of the Θ factors were calculated with Lu's curves [5] and the Fourier calculations were facilitated with Hägg-Laurent's calculating machine [6].

SYMMETRY AND UNIT CELL DIMENSIONS

In Weissenberg photographs no deviation from orthorhombic symmetry could be observed. In order to determine the symmetry, the powder photographs were analyzed in detail. The values of the unit cell dimensions given by Magnéli corresponding to monoclinic symmetry, and those given by Wyart and Foëx corresponding to triclinic symmetry, were tested. It was found that all lines in the powder photographs could be indexed by means of a monoclinic quadratic form (*Cf.* Table 1).

In Table 2 the values of the unit cell dimensions obtained in the present investigation are compared with those given by earlier investigators.

The Laue symmetry of WO_3 must clearly be $2/m$. Reflections $(h0l)$ were all absent when $h = 2n + 1$, and reflections $(0k0)$ were only observed when $k = 2n$; these absences are characteristic of the space-group $C_{2h}^5 - P2_1/a$. In fact, Braekken's co-ordinates correspond to this symmetry.

ATOMIC POSITIONS

A calculation of the structure factors, based on Braekken's co-ordinates for the tungsten positions, showed good agreement with the observed data. The signs of the F values obtained in this connection were used together with the intensities now obtained from the Weissenberg photographs for a calculation of the electron density function. The x and y parameters were determined from the projection of the electron density along the c-axis, and the z parameter and a control of the y parameter were obtained from the section $\varrho\ (\frac{1}{4}, y, z)$. The data thus obtained completely confirm Braekken's values, as can be seen from Table 3.

The tungsten atoms are thus in principle arranged as in the ReO_3 structure, but their distances show certain variations, *viz.*

3.705 Å approximately in the direction of the a-axis
3.79 Å » » » » » » b- »
3.835 Å in the direction of the c-axis

The positions of the oxygen atoms could not be determined from X-ray data. If the symmetry of the arrangement of the oxygen atoms is the same as that deduced for the tungsten atoms, 4 oxygen atoms must occupy the parameter-free positions 2 (a) and 2 (c). Concerning the other oxygen atoms, no

Table 1. Powder photograph data for tungsten trioxide Cu-Ka-radiation.

h k l	I_{rel}	$\sin^2\Theta$ obs	$\sin^2\Theta$ calc	h k l	I_{rel}	$\sin^2\Theta$ obs	$\sin^2\Theta$ calc
001	100	.0405	.0404	421	35	.2644	.2645
020	95	.0420	.0421	$13\bar{2}$	25	.2663	.2663
200	100	.0448	.0448	132			.2690
011	5	.0511	.0510	$31\bar{2}$	60	.2691	.2691
120	50	.0532	.0533	340			.2692
$11\bar{1}$	50	.0615	.0615	312	35	.2771	.2771
111	50	.0628	.0628	$23\bar{2}$	10	.2986	.2986
021	75	.0825	.0825	$32\bar{2}$	5	.3008	.3006
$20\bar{1}$	60	.0839	.0839	051	20	.3037	.3035
201	90	.0868	.0866	232			.3039
220			.0869	$34\bar{1}$	25	.3077	.3076
$12\bar{1}$	35	.0930	.0930	341	25	.3114	.3116
121	40	.0944	.0944	520	10	.3222	.3222
$22\bar{1}$	50	.1260	.1260	$51\bar{1}$	5	.3277	.3278
221	60	.1286	.1287	042	25	.3299	.3300
031	10	.1351	.1351	511	25	.3356	.3345
320	40	.1430	.1429	$40\bar{2}$			.3356
$13\bar{1}$	30	.1456	.1457	$14\bar{2}$	10	.3399	.3399
131	25	.1471	.1470	142	10	.3427	.3426
$31\bar{1}$	35	.1499	.1498	402	45	.3475	.3464
311	30	.1538	.1538	440			.3476
002	50	.1617	.1617	$33\bar{2}$	20	.3534	.3532
040	50	.1683	.1683	332	15	.3609	.3613
400	75	.1794	.1793	$24\bar{2}$	15	.3720	.3722
140			.1796	242	30	.3777	.3776
$11\bar{2}$	40	.1822	.1821	$42\bar{2}$			.3777
112	50	.1848	.1848	$11\bar{3}$	20	.3833	.3836
$20\bar{2}$	60	.2038	.2038	$44\bar{1}$	20	.3851	.3854
022			.2038	113	20	.3875	.3876
041	55	.2088	.2088	422			.3884
202			.2092	160	40	.3898	.3900
240	50	.2132	.2132	441			.3907
$40\bar{1}$	40	.2172	.2171	600	20	.4033	.4034
$14\bar{1}$	25	.2193	.2193	$53\bar{1}$	5	.4119	.4119
141	65	.2214	.2207	531	5	.4187	.4186
420			.2214	260	10	.4242	.4236
401			.2224	052			.4247
$33\bar{1}$	10	.2341	.2340	$34\bar{2}$	5	.4266	.4269
331	10	.2380	.2380	$16\bar{1}$	20	.4293	.4297
$22\bar{2}$	30	.2460	.2459	$43\bar{2}$	25	.4306	.4304
222	40	.2513	.2513	161			.4311
$24\bar{1}$		.2522	.2523	$15\bar{2}$	10	.4346	.4346
241	25	.2548	.2549	342			.4349
$42\bar{1}$	45	.2592	.2591	152	5	.4369	.4373

Table 1. continued.

$h\ k\ l$	I_{rel}	$\sin^2\Theta$ obs	$\sin^2\Theta$ calc	$h\ k\ l$	I_{rel}	$\sin^2\Theta$ obs	$\sin^2\Theta$ calc
$60\bar{1}$	15	.4397	.4398	360	20	.4790	.4796
432	5	.4412	.4411	$45\bar{1}$			.4801
620	30	.4453	.4455	313	30	.4809	.4812
601			.4479	$62\bar{1}$			.4819
540	25	.4483	.4485	451			.4854
033	20	.4587	.4585	$54\bar{1}$	5	.4858	.4856
$25\bar{2}$			.4669	621	10	.4895	.4900
$13\bar{3}$	10	.4671	.4677	541	15	.4918	.4923
$31\bar{3}$	20	.4689	.4692	630			.4981
133			.4718	$23\bar{3}$	10	.4983	.4993
252	25	.4714	.4722				

definite conclusions can be drawn. They may be situated half way between neighbouring tungsten atoms in accordance with Braekken's assumption. In this connection it may be mentioned that, in molybdenum oxides where MoO_6 octahedra exist which do not share edges with adjacent octahedra, the former are rather distorted. This has been demonstrated in the oxides Mo_8O_{23} and Mo_9O_{26} [8].

Table 2. Unit cell dimensions.

Authors	a Å	b Å	c Å	α	β	γ
Braekken [1]	7.28	7.48	3.82	90°	~90°	90°
Magnéli [3]	7.29	7.54	3.85	90°	90.9°	90°
Ueda and Ichinokawa [7]	7.278	7.460	3.838	90°	~90°	90°
Wyart and Foëx [4]	7.21	7.44	3.80	90.25°	90.02°	90.50°
The present investigation	7.285	7.517	3.835	90°	90.90°	90°

Table 3. Atomic parameters for tungsten.

Authors	4W in 4 (*e*) x	y	z
Braekken [1]	0.250	0.031	0.063
The present investigation	0.250	0.032	0.062

SUMMARY

The crystal structure of WO_3 was investigated. The symmetry has been found to be monoclinic (pseudoorthorhombic) and belonging to the space-

group $C_{2h}^5-P2_1/a$. The positions of the tungsten atoms given by Braekken have been verified with Fourier methods.

The author wishes to thank Professor G. Hägg and Dr. A. Magnéli for their kind interest in this investigation. A grant from the *Swedish Natural Science Research Council* is gratefully acknowledged.

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Received June 25, 1952.