Discussion

At room temperature the B.D.H. sample is orthorhombic. Its lattice constants are

$$a = 10{\cdot}4,\ b = 8{\cdot}73,\ c = 7{\cdot}4\ \text{Å}.$$

On chemical analysis it was found to be aluminium arsenate octahydrate (Sharan, 1959). When heated to 900 °C. it proved to be completely identical with that of Machatschki.

The laboratory sample on the other hand shows certain striking features. The compound as prepared has two properties in common with that of Strada. It is amorphous at low temperatures and becomes crystalline on heating it to about 850 °C. But it differs from that of Strada in that it does not show any crystalline nature on heating to 550 °C. The modification obtained at about 850 °C. is entirely different from that reported by Strada. The $\sin^2\theta$ values and the intensities are different for both. The new modification has been indexed by using Lipson's and Vand's method, by taking

$$\lambda^2/4a^2 = A = 0{\cdot}0050,\ \lambda^2/4b^2 = B = 0{\cdot}0074,\ \lambda^2/4c^2 = C = 0{\cdot}0088.$$

The cell turns out to be orthorhombic with lattice constants as

$$a = 10{\cdot}90,\ b = 8{\cdot}96,\ c = 8{\cdot}22\ \text{Å}.$$

The validity of the lattice constants is apparent from the good agreement between the observed and calculated $\sin^2\theta$ values as given in Table 1.

Table 1. *Powder photograph data for the new modification of aluminium ortho-arsenate*

$\sin^2\theta$ (obs.)	$\sin^2\theta$ (calc.)	*hkl*
0·0197	0·0200	200
0·0287	0·0288	101
	0·0296	020
0·0494	0·0496	220
0·0718	0·0716	130
0·0790	0·0792	003
0·0882	0·0888	410
0·0999	0·0992	203
0·1107	0·1106	420
0·1477	0·1466	430
0·1565	0·1555	431
0·1641	0·1634	340
0·1821	0·1818	432
0·2023	0·2024	143
0·2263	0·2274	510
		234
0·2490	0·2496	025
0·2727	0·2792	244
0·2811	0·2802	161
		702
0·3057	0·3066	162
		235
0·3572	0·3584	245
		821
0·3765	0·3764	171
0·4527	0·4524	734
0·4869	0·4876	750
0·5540	0·5546	147
0·5841	0·5832	066
0·6037	0·6026	275
0·6309	0·6298	038
0·6597	0·6594	384
0·6857	0·6866	148

Strada has not stated anything about the stability of his sample. The present laboratory sample heated to about 850 °C. has proved to be unstable. It could not retain its structure even for three days. During this time it must have undergone a number of crystallographic transformations. Preliminary studies show that the transformations depend largely upon (1) the amount of water of crystallisation, (2) the thermal history and (3) the temperature. Detailed studies are in progress and will be reported in due course.

The work was carried out in the Laboratory of the Banaras Hindu University under the supervision of Dr B. Dayal to whom the author's thanks are due. The author is also grateful to Dr K. S. Krishnan, F.R.S. for his active interest in the work.

References

MACHATSCHKI, F. (1935). *Z. Kristallogr.* A, **90**, 314.
MACHATSCHKI, F. (1936). *Z. Kristallogr.* A, **94**, 222; Fortsch. *Min. Krist.* **20**, 45.
SCHULZE, G. E. R. (1934). *Z. Phys. Chem.* (B), **24**, 215; *Strukturbericht* III, 423.
SHARAN, B. (1959). *Proc. Nat. Inst. Sci.* In press.
STRADA, M. (1934). *Gazz. Chim. Ital.* **64**, 653.

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A new interpretation of the X-ray diffraction pattern of mallinckrodt UO_3.

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Mallinckrodt UO_3 has been studied by Perio (1953) who states that the unit cell is orthorhombic with dimensions

$$a = 12{\cdot}98,\ b = 10{\cdot}70,\ c = 7{\cdot}49\ \text{Kx}.$$

Although the agreement between calculated and observed values of $1/d^2$ is good, one is suspicious of this structure because of the exceedingly large proportion of absent lines. Further doubt arises when attempts are made to index higher-angle lines, when the agreement between observed and calculated values of $1/d^2$ becomes increasingly bad. From these observations, it was decided that Perio's structure was incorrect. It has been reported that some summation relations exist between pairs of $\sin^2\theta$ values which indicate that the compound may be monoclinic (Dawson *et al.*, 1956).

The sample of UO_3 was prepared by oxidation of U_3O_8 at 700 °C. under 150 atm. oxygen, and the X-ray diffraction pattern was produced using a Guinier-type focusing camera with monochromatized Cu $K\alpha$ radiation.

Examination of the diffraction pattern revealed several

Table 1. *Calculated and observed X-ray data*

$d(hkl)$ (Å)	I/I_0	$\sin^2\theta$ (obs.)	$\sin^2\theta$ (calc.)	(hkl)
6·533	*m*	0·0139	0·0139	200
4·992	*s*	238	239	220
			258	121
4·784	*w*	259	259	130
			260	12$\bar{1}$
4·396	*s*	307	309	211
4·368	*s*	312	313	21$\bar{1}$
3·445	*vs*	500	500	002
			557	141
			557	400
3·253	*vs*	560	558	112
			559	14$\bar{1}$
			561	11$\bar{2}$
			633	122
3·052	*s*	635	636	12$\bar{2}$
			636	202
3·037	*s*	643	643	20$\bar{2}$
2·798	*s*	758	757	132
2·788	*s*	761	760	13$\bar{2}$
			762	250
			781	151
2·753	*m*	783	781	430
			783	15$\bar{1}$
			785	42$\bar{1}$
2·629	*m*	858	860	232
			1032	332
2·393	*vvw*	1036(*B*)	1035	242
			1035	260
			1041	24$\bar{2}$
2·202	*w*	1224	1224	023
			1224	53$\bar{1}$
			1254	170
2·175	*w*	1255	1254	600
			1256	123
			1258	252
2·130	*w*	1303	1301	451
2·122	*w*	1310	1308	45$\bar{1}$
2·107	*w*	1337	1337	36$\bar{1}$
			1358	223
2·091	*m*	1357	1359	270
			1362	502
			1453	460
2·016	*vw*	1459(*B*)	1455	313
			1461	522
			1463	44$\bar{2}$
1·995	*vw*	1491	1486	27$\bar{1}$
			1493	550
1·912	*m*	1622	1622	55$\bar{1}$
			1628	180
			1652	640
1·895	*m*	1652	1654	333
			1655	371
1·868	*w*	1741	1743	602
			1754	18$\bar{1}$
1·836	*w*	1760	1760	542
			1764	60$\bar{2}$
			1767	560
			1768	612
1·830	*w*	1771(*B*)	1771	423
			1772	641
			1777	470
			1777	54$\bar{2}$

$d(hkl)$ (Å)	I/I_0	$\sin^2\theta$ (obs.)	$\sin^2\theta$ (calc.)	(hkl)
			1784	15$\bar{3}$
1·821	*w*	1788	1789	61$\bar{2}$
			1792	42$\bar{3}$
1·788	*w*	1856	1859	28$\bar{1}$
			1891	253
1·769	*m*	1896	1896	56$\bar{1}$
			1898	47$\bar{1}$
1·760	*w*	1914	1916	43$\bar{3}$
1·745	*w*	1947	1946	462
1·739	*vw*	1964	1960	46$\bar{2}$
			1967	632
			1996	651
1·721	*w*	2000(*B*)	1999	004
			2001	55$\bar{2}$
			2006	65$\bar{1}$
1·709	*vvw*	2031	2029	381
			2031	104
1·677	*m*	2109	2105	740
			2108	52$\bar{3}$
			2155	263
1·658	*w*	2158	2155	290
			2157	214
			2161	64$\bar{2}$
1·631	*m*	2229	2229	800
			2320	72$\bar{2}$
			2323	30$\bar{4}$
			2326	363
1·597	*s*	2326	2327	314
			2329	750
			2329	820
			2330	390
			2489	0,10,0
1·542	*vw*	2490	2489	27$\bar{3}$
			2494	62$\bar{3}$
1·532	*m*	2529	2524	1,10,0
			2530	244
			2543	24$\bar{4}$
1·527	*w*	2545	2543	404
			2547	33$\bar{4}$
			2568	414
1·519	*m*	2569	2568	463
			2570	40$\bar{4}$
			2573	490
1·472	*vw*	2740	2740	812
			2767	434
1·464	*m*	2767	2768	25$\bar{4}$
			2768	81$\bar{2}$
			2846	910
1·442	*w*	2853	2852	283
			2852	850
			2853	504
			2939	832
1·419	*w*	2944	2941	444
			2945	35$\bar{4}$
			2949	72$\bar{3}$
			2984	67$\bar{2}$
1·408	*vw*	2991	2987	52$\bar{4}$
			2989	0,10,2
			3073	73$\bar{3}$
1·389	*vvw*	3076	3077	534
			3080	49$\bar{2}$
1·369	*w*	3165	3165	454

[(*B*) indicates broad, diffuse line.]

split lines, suggesting a monoclinic or triclinic unit cell. It proved possible to index the film in terms of a monoclinic unit cell having the dimensions

$$a = 13{\cdot}05 \pm 0{\cdot}02,\ b = 15{\cdot}45 \pm 0{\cdot}05,\ c = 6{\cdot}89 \pm 0{\cdot}02\ \text{Å};$$
$$\beta = 89{\cdot}63 \pm 0{\cdot}01°.$$

Observed and calculated values of $\sin^2\theta$ are given in Table 1.

Although this interpretation gives only about one quarter of the lines present (Perio's gave less than one tenth), it is felt that it can be accepted in the absence of a better one, as the cell is large and asymmetric and the pattern is rather diffuse.

The evidence for the space group is not very conclusive. For $P2_1/c$ symmetry, $(h0l)$ reflections are absent if l is odd. It is not possible to say whether (201), (203) and $(10\bar{5})$ are present or not as these reflections would occur at $\sin^2\theta = 0{\cdot}0262$, $0{\cdot}1259$ and $0{\cdot}3163$ at which points several other reflections coincide (see Table 1). The other systematic absence to be expected is $(0k0)$ with k odd. In fact, only one $(0k0)$ reflection was observed, (0,10,0), although the others do not coincide with other lines. It is possible that $(h0l)$ is also absent when h is even. However, this is not a space-group extinction and, if this absence is real, it is probably due to some special arrangement of the uranium atoms. It is calculated from density measurements that there are 22 formula UO_3 per unit cell, but this must be either 20 or 24 for reasons of symmetry. As 24 units can be fitted into the unit cell, this value is favoured.

In the absence of a single crystal, no further work on this compound is contemplated.

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References

Dawson, J. K., Wait, E., Alcock, K. & Chilton, D. R. (1956). *J. Chem. Soc.* 683, 3540.
Perio, P. (1953). *Bull. societé chim. Fr.*, p, 776.

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The crystal structure of ZrO_2 and HfO_2.

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McCullough & Trueblood (1959) pointed out that the crystal structure of baddeleyite (monoclinic ZrO_2) as determined by Náray-Szabó (1936) is not correct and published a new description of the structure based on single-crystal data obtained from a natural crystal.

Approximately a year ago while working on the irradiation induced phase transformations in ZrO_2 (Adam & Cox) we have also concluded that the accepted Náray-Szabó structure is wrong and made accurate X-ray intensity measurements on chemically prepared ZrO_2 and HfO_2 powder with a counter diffractometer and monochromatic copper $K\alpha$ radiation. Using atomic parameters proposed by McCullough & Trueblood (1959) a satisfactory agreement was obtained between calculated and observed F^2 values for both materials although a few minor discrepancies have been found. This indicates that HfO_2 and ZrO_2 are isomorphous and their structure is basically the same as that of naturally occurring baddeleyite. The following unit-cell dimensions have been determined using a Guinier-type focusing camera:

	a (Å)	b (Å)	c (Å)
ZrO_2	$5{\cdot}1454 \pm 0{\cdot}0005$	$5{\cdot}2075 \pm 0{\cdot}0005$	$5{\cdot}3107 \pm 0{\cdot}0005$
	β		
	$99° 14' \pm 0° 05'$		
	a (Å)	b (Å)	c (Å)
HfO_2	$5{\cdot}1156 \pm 0{\cdot}0005$	$5{\cdot}1722 \pm 0{\cdot}0005$	$5{\cdot}2948 \pm 0{\cdot}0005$
	β		
	$99° 11' \pm 0° 05'$		

References

Adam, J. & Cox, B. *J. Nucl. Energy.* To be published.
McCullough, J. D. & Trueblood, K. N. (1959). *Acta Cryst.* **12**, 507.
Náray-Szabó, St. V. (1936). *Z. Kristallogr.* **94**, 414.

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International Union of Crystallography

Fedorov Commemoration, Leningrad, 21–27 May 1959

By invitation of the Academy of Sciences of the U.S.S.R., the Union participated in two Symposia which were held in Leningrad, U.S.S.R., from 21 to 27 May 1959 in commemoration of the 40th anniversary of the death of the great Russian crystallographer E. S. Fedorov. Under the auspices of the Union and the Academy, the meetings were organized by the U.S.S.R. National Committee for Crystallography in cooperation with the Institute of Crystallography of the Academy of Sciences, the Mineralogical Society of the U.S.S.R., the Leningrad Institute of Mines, and the Fedorov Institute of Crystallography, Mineralogy and Petrography.

Over eight hundred crystallographers and other scientists, mainly from the U.S.S.R., and in addition from fifteen other countries, participated in the meetings. The attendance of several of these scientists from abroad