

similar state in Zr_4Al_3 (Wilson, Thomas & Spooner, 1959). Such Zr atoms have a Z-14 triangulated co-ordination shell and according to Frank & Kasper (1959), the apparent compression is to be expected. It is rather surprising to note that aluminium can behave like silicon in forming a Nowotny phase with zirconium and this seems to suggest that packing is the most important factor affecting the appearance of this phase.

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A new modification of aluminium ortho-arsenate. By B. SHARAN, *Department of Physics, Banaras Hindu University, India*

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There is a controversy in the literature between Strada (1934) and Machatschki (1935) about the structure of aluminium ortho-arsenate. The former has reported a tetragonal structure with cell constants $a = 4.90$, $c = 6.64$ Å, while the latter has reported a hexagonal structure with $a = 5.03$, $c = 11.22$ Å. The complete structure of the tetragonal form has been worked out by Schulze (1934) and that of the hexagonal form by Machatschki (1936) himself. The latter has strongly criticised Strada's work and has expressed an opinion that a tetragonal structure of this compound cannot possibly exist. He has advanced the argument that the density calculated from the hexagonal cell was in better accord with the experimental values than that calculated from Strada's work. He has also pointed out that the As-O distance worked out by Schulze (1935) for the tetragonal structure is higher than is usually obtained.

If one examines Strada's data as quoted by Machatschki in his paper and compares it with that of his own it becomes apparent that the latter's criticism has no force. The observed intensities and the $\sin^2 \theta$ values of the two workers are entirely different, and the density was not measured independently by Machatschki but was taken from the work of Strada. The latter has claimed a high degree of accuracy for his work and it seems more reasonable to assume that the two were working with two different modifications of the same compound. It

was therefore decided to reinvestigate the matter and obtain the two forms separately. In the course of investigations a sample of aluminium ortho-arsenate was prepared by a process only slightly different from the one used by Strada. The study of this revealed a third and new form of this compound which has an *orthorhombic* structure. These results are presented here.

Experimental

In the present investigations two samples of aluminium ortho-arsenate were used. One was procured from the British Drug House (called B.D.H. sample), and the other (called laboratory sample) was obtained as a gelatinous precipitate from aluminium alum by the use of potassium di-arsenate. The excess of the sulphuric acid produced in the reaction was neutralized by sodium acetate. This method is the same as that used by Strada, except that he used sodium di-arsenate instead of the potassium compound. For X-ray work the laboratory sample was heated in two silica crucibles for 8 hr.; in one the temperature was kept at 550 °C., and in the second it ranged between 850 and 900 °C. The X-ray photographs were taken on a Philips Debye-Scherrer camera using $Cu K\alpha$ radiation and Straumanis' mounting. All the heated samples were air-quenched before mounting in the camera. The following results were obtained.

Sample	Nature of the photograph	Inference	Remarks
<i>B.D.H. sample</i>			
1. At room temp.	Many lines	Crystalline	Al. arsenate octahydrate
2. Heated at 900 °C.	Many lines	Crystalline	Hexagonal form identical with that of Machatschki
<i>Lab. sample</i>			
3. Unheated	Weak halo	Amorphous	
4. Heated at 550 °C. and air quenched	Broad halo at $\theta = 11^\circ$	Amorphous	
5. Heated at 850-900 °C. and air quenched	Many lines	Crystalline orthorhombic	New modification
6. Same as above after 3 days	Broad halo at $\theta = 14.5^\circ$	Amorphous	

Discussion

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

$$a = 10.4, b = 8.73, c = 7.4 \text{ \AA}.$$

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

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

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A new interpretation of the X-ray diffraction pattern of mallinckrodt UO_3 . By DAVID E. CONNOLLY, *United Kingdom Atomic Energy Authority, Springfields Works, Salwick, Nr. Preston, Lancs, England*

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

$$a = 12.98, b = 10.70, c = 7.49 \text{ Kx.}$$

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 in-

creasingly 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).

$$\lambda^2/4a^2 = A = 0.0050, \lambda^2/4b^2 = B = 0.0074, \lambda^2/4c^2 = C = 0.0088.$$

The cell turns out to be orthorhombic with lattice constants as

$$a = 10.90, b = 8.96, c = 8.22 \text{ \AA}.$$

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.

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.

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