Acta Cryst. (1959). **12**, 947

The crystal structure of Zr_5Al_3.

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(*Received* 30 *July* 1959)

The crystal structure of the alloy Zr_5Al_3 has been determined by powder techniques. The bulk specimen was prepared by Miss J. Murray of A.E.R.E., Harwell, by arc melting in argon and contained 12·5% by weight of aluminium. The identity of the phase was established with 19 cm. powder photographs; the film used in the solution of the structure was taken by Dr J. Adam at A.E.R.E., Harwell, with a focusing camera using monochromatic Cu K radiation. The film was measured on a Cambridge universal measuring instrument and line intensities were estimated visually. The values of $\sin^2\theta$ and the observed and calculated intensities are given in Table 1.

Table 1. *X-ray data*

	$\sin^2\theta$ ($\times 10^4$)		Relative intensities	
hkil	Observed	Calculated	Observed	Calculated
$10\bar{1}0$	118	118	*vvw*	0·1
$11\bar{2}0$	354	355	*m*	12·9
$20\bar{2}0$	472	473	*ms*	20·7
$11\bar{2}1$	537	538	*ms*	24·2
0002	730	731	*vw*	7·1
$21\bar{3}0$	827	829	*s*	52·5
$10\bar{1}2$	849	849	*s*	41·3
········	········	········	········	········
$21\bar{3}1$	1008	1009	*vvs*	97·1
$30\bar{3}1$	1063	1062	*ms*	24·8
$11\bar{2}2$	1084	1085	*s*	66·3
$20\bar{2}2$	—	1204	—	2·2
$22\bar{4}0$	1417	1417	*vvw*	2·4
$31\bar{4}0$	1535	1535	*vvw*	2·4
$21\bar{3}2$	1556	1557	*vvw*	0·7
$22\bar{4}1$	1599	1599	*w*	6·3
$30\bar{3}2$	1791	1793	*w*	5·9
$40\bar{4}0$	1887	1889	*vw*	4·1
$11\bar{2}3$	1997	1998	*mw*	3·5
$22\bar{4}2$	2145	2147	*ms*	21·6
$32\bar{5}0$	2240	2243	*vw*	3·8
$31\bar{4}2$	2264	2265	*vw*	6·6
$32\bar{5}1$	2426	2426	*w*	7·9
$21\bar{3}3$	2468	2470	*ms*	25·3
$41\bar{5}0$	2478	2479	*ms*	22·4
$40\bar{4}2$	2618	2619	*ms*	23·3
0004	2922	2922	*vw*	8·1
$50\bar{5}0$	2951	2951	*vvw*	2·9
$22\bar{4}3$	3057	3060	*vvw*	2·2
$42\bar{6}0$	3305	3305	*vw*	5·4
$33\bar{6}1$	3368	3370	*w*	10·4
$20\bar{2}4$	—	3395	—	2·1
$51\bar{6}0$	3661	3659	*vvw*	1·6
$50\bar{5}2$	3684	3682	*m*	16·0
$21\bar{3}4$	3752	3749	*w*	9·8
$51\bar{6}1$	3848	3842	*vvw*	1·6
$32\bar{5}3$	3890	3887*	*w*	3·6
$33\bar{6}2$	3923	3918	*w*	11·7
$30\bar{3}4$	3987	3985	*vw*	5·9
$51\bar{6}2$	—	4399	—	2·6
$52\bar{7}1$	4790	4787	*vvw*	3·3

* Line overlaps line of neighbouring phase.

All values of $\sin^2\theta$ below dotted line refer to α_1 components.

vvs—very very strong; *vs*—very strong; *s*—strong; *ms*—medium strong; *mw*—medium weak; *w*—weak; *vw*—very weak; *vvw*—extremely weak.

According to the thermal equilibrium diagram for the zirconium–aluminium system (McPherson & Hansen, 1951) Zr_5Al_3 is unstable at normal temperatures and when formed from the melt it is thought to decompose into Zr_2Al and Zr_3Al_2. It was not surprising, therefore, that the powder film showed the presence of both of these phases. The presence of the other phases was confirmed by a metallographic examination of a polished specimen. It was found that all the stronger lines of the film and many others could be indexed as a hexagonal unit cell whose dimensions were:

$$a = 8{\cdot}184 \pm 0{\cdot}002 \quad \text{and} \quad c = 5{\cdot}702 \pm 0{\cdot}002 \text{ Å}; \quad c/a = 0{\cdot}697 .$$

On the assumption that this was the cell of Zr_5Al_3 and that the atom sizes were essentially those of the pure elements the calculated density with two units of Zr_5Al_3 in the cell is 5·393 g.cm.$^{-3}$. The density of the specimen measured with a specific gravity bottle was 5·61 g.cm.$^{-3}$.

The only extinctions observed were those of $hh0l$ when l was odd. This led to the possibility that the structure has the space group D_{6h}^3–$P6_3/mcm$ and is isomorphous with Mn_5Si_3 which has the $D8_8$-type structure. This was found to be so and a reasonable intensity agreement is found with the following atomic positions:

6 Zr (g) $x, 0, \frac{1}{4}$ with $x = 0{\cdot}23$
4 Zr (d) $\frac{1}{3}, \frac{2}{3}, 0$
6 Al (g) $x, 0, \frac{1}{4}$ with $x = 0{\cdot}59$.

With these atomic positions the inter-atomic distances are as follows:

Zr–2 Zr	2·85 Å
Zr–2 Zr	3·42
Zr–2 Zr	3·26
Zr–6 Zr	3·53
Zr–1 Al	2·95
Zr–2 Al	2·91
Zr–6 Al	2·86
Al–1 Al	3·21

Discussion

The $D8_8$ structure described above is associated with the A_5B_3 phase formed by a transition element as atom A and an element such as silicon, tin, germanium, etc., from group IVb of the periodic table, as atom B. Such compounds, which are sometimes known as Nowotny phases have been reported for zirconium with silicon, tin and lead (Schachner, Nowotny & Machenschalk, 1953). This phase is characterized by rows of equally spaced atoms of the transition element lying along the 6-fold axes of the unit cell, all the other atoms lying in the vertical faces of the cell forming triangular enclosures around the axial atoms. The closest distances between the axial Zr atoms and other Zr atoms are generous compared with the interatomic distance in the elementary form, but the distance between axial atoms (2·85 Å) shows a fairly large compression. Thus, the Zr atoms along the 6-fold axes behave like oblate spheres with respect to neighbouring Zr atoms, as was noted for the Zr atoms in a 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.

The authors wish to thank Dr J. Adam of A.E.R.E., Harwell, for advice and encouragement and Mr H. D. Mallon, R.M.C.S., Shrivenham, for assistance in the metallurgical examination. Permission to publish this paper has been granted by the Dean, R.M.C.S., Shrivenham.

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Acta Cryst. (1959). **12**, 948

A new modification of aluminium ortho-arsenate.

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(*Received* 17 *August* 1959)

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
B.D.H. sample			
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
Lab. sample			
3. Unheated	Weak halo	Amorphous	
4. Heated at 550 °C. and air quenched	Broad halo at $\theta = 11°$	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 $\theta = 14.5°$	Amorphous	