

57-162 mm. having been determined by calibration with sodium chloride. The dimensions of the unit cell were found to be:

$$a_0 = 7.37 \pm 0.02, \quad b_0 = 4.60 \pm 0.02, \quad c_0 = 14.34 \pm 0.03 \text{ \AA};$$

$$\beta = 108^\circ 59' \pm 8'.$$

These data give the axial ratios: $a:b:c = 1.602:1:3.118$.

The observed density of 1.42 g.cm.^{-3} agrees well with the density of 1.417 g.cm.^{-3} calculated on the basis of two formula units per unit cell.

When the diffraction spots in the Weissenberg and

precession photographs were indexed the following interferences were observed: hkl in all orders; $h0l$ when $l=2n$; $0k0$ when $k=2n$. These data are consistent with the space group $C_{2h}^2-P2_1/c$. Structural investigations on 5-oxiphenazine and 5-10-dioxiphenazine are in progress.

Reference

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The crystal structure of Zr_4Al_3 . By C. G. WILSON, D. K. THOMAS and F. J. SPOONER, *Royal Military College of Science, Shrivenham, Berks, England*

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The crystal structure of the intermetallic compound Zr_4Al_3 has been determined from powder photographs. Powder specimens were obtained by filing from a solid sample of the alloy prepared by arc melting in argon by Miss J. Murray, A.E.R.E., Harwell. Microscopic examination of a polished surface of the solid sample shewed it to be mainly single phase. The photographs

obtained with a precision 19 cm. camera (Adam, 1954) gave fairly broad lines with a heavy background caused by the Zr $K\alpha$ radiation excited by the continuous spectrum of the Cu target. Whilst these photographs enabled a unit cell to be determined, more accurate measurements of line spacings and intensities were made on a photograph taken by Dr J. Adam with a focusing camera using monochromatised Cu $K\alpha$ radiation. An attempt was made to find single crystals of suitable size in a crushed specimen, but this proved impossible. The values of $\sin^2 \theta$ obtained from measurements made with a Cambridge universal measuring machine and the visual estimate of line intensities is given in Table 1.

Several weak and very weak lines appearing on the focusing camera film have been shown to belong to a neighbouring phase in the Zr-Al system. All the remaining lines have been indexed on a hexagonal unit cell with:

$$a = 5.433 \pm 0.002, \quad c = 5.390 \pm 0.002 \text{ \AA}.$$

Assuming that the volumes occupied by the individual atoms in the alloy are not appreciably different from those occupied by these atoms in the elements, the number of formula units of Zr_4Al_3 per unit cell is unity. On this basis the calculated density is 5.37 g.cm.^{-3} . The density of the solid sample determined using a specific-gravity bottle was 5.28 g.cm.^{-3} .

No systematic absences were observed and packing considerations led to a choice of space group $C_{2h}^2-P\bar{6}$. The calculated line intensities shown in Table 1 are obtained with the atoms in the following positions:

$$3 \text{ Al } 2(j) \quad x, y, 0; \text{ with } x = \frac{1}{3}, y = \frac{1}{3}.$$

$$2 \text{ Zr } 3(h) \quad \frac{1}{3}, \frac{2}{3}, z; \text{ with } z = \frac{1}{4}.$$

$$1 \text{ Zr } \bar{6}(f) \quad \frac{2}{3}, \frac{1}{3}, \frac{1}{2}.$$

$$1 \text{ Zr } \bar{6}(b) \quad 0, 0, \frac{1}{2}.$$

The interatomic distances are as follows:

$$(6) \text{ Al-Zr } \quad 3.03 \text{ \AA}$$

$$(6) \text{ Zr-Zr } \quad 3.41$$

$$(1) \text{ Zr-Zr } \quad 2.70$$

$$(2) \text{ Al-Al } \quad 2.72$$

Table 1. X-ray data

(hkl)	$\sin^2 \theta$ (obs.)	$\sin^2 \theta$ (calc.)	Intensities (obs.)	Intensities (calc.)
0001	0.0204	0.0204	m	2.3
10 $\bar{1}$ 0	0.0268	0.0268	m	2.7
10 $\bar{1}$ 1	0.0472	0.0473	m	2.9
11 $\bar{2}$ 0	0.0805	0.0805	vs	18.4
0002	0.0817	0.0818	vw	0.4
11 $\bar{2}$ 1	0.1009	0.1010	vs	10.3
20 $\bar{2}$ 0	0.1073	0.1074	ms	3.1
10 $\bar{1}$ 2	0.1086	0.1086	vs	19.0
20 $\bar{2}$ 1	0.1277	0.1278	ms	4.9
20 $\bar{2}$ 2	0.1887	0.1888	m	3.3
21 $\bar{3}$ 1	0.2079	0.2080	vw	0.6
10 $\bar{1}$ 3	0.2104	0.2105	vw	0.3
30 $\bar{3}$ 0	0.2412	0.2412	m	3.4
30 $\bar{3}$ 1	0.2615	0.2616	m	2.3
11 $\bar{2}$ 3	0.2640	0.2614	m	2.2
21 $\bar{3}$ 2	0.2692	0.2692	s	8.9
20 $\bar{2}$ 3	0.2909	0.2909	w	1.3
22 $\bar{4}$ 0	0.3216	0.3216	m	3.6
0004	0.3267	0.3266	vw	1.2
22 $\bar{4}$ 1	0.3422	0.3420	vw	0.3
31 $\bar{4}$ 1	0.3684	0.3688	vw	0.2
21 $\bar{3}$ 3	0.3711	0.3713	vw	0.2
22 $\bar{4}$ 2	0.4034	0.4032	vw	0.16
11 $\bar{2}$ 4	0.4071	0.4070	m	2.9
30 $\bar{3}$ 3	0.4250	0.4249	vw	1.0
31 $\bar{4}$ 2	0.4302	0.4299	ms	4.1
20 $\bar{2}$ 4	0.4339	0.4336	vw	0.6
40 $\bar{4}$ 1	0.4490	0.4492	vw	0.7
40 $\bar{4}$ 2	0.5105	0.5104	w	0.8
0005				
31 $\bar{4}$ 3	0.5323	0.5321	vw	0.16

vs=very strong; s=strong; ms=medium strong;

m=medium; w=weak; vw=very weak;

vwv=very very weak; vwv=extremely weak.

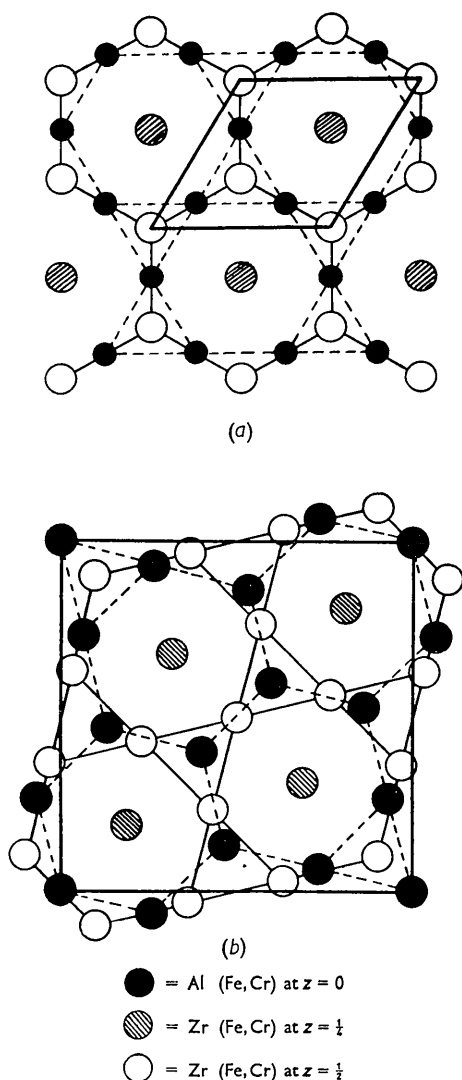


Fig. 1. Structure of (a) Zr_4Al_3 and (b) σ -phase (Fe-Cr).

The proposed structure bears a close resemblance to the σ -phase structure of the transition elements. A section of the structure viewed along the c -axis is shown in Fig. 1, together with a similar section of the σ -phase of Fe-Cr. In the σ -phase the two layers of atoms having pseudo-hexagonal symmetry have their hexagonal axes displaced relative to each other, whilst the corresponding layers of alternate Zr and Al atoms in the Zr_4Al_3 structure

are symmetrically disposed relative to each other about the common hexagonal axis.

The Zr atoms in the $\frac{1}{3}, \frac{2}{3}, \pm \frac{1}{4}$ positions form an unbroken chain as in the σ -phase. The distance between the Zr atoms in this chain is 2.7 Å, which is much less than the normal 12-co-ordination interatomic distance (3.2 Å approx.) for Zr. This atomic compression, which is also apparent in the σ -phase, may possibly be explained by the comparative isolation of the similar chains of atoms.

Discussion

It is interesting to note that the Zr_4Al_3 structure is identical with the structure for A_4B_3 alloys postulated by Frank & Kasper in a recent paper (Frank & Kasper, 1959). In their paper Frank & Kasper discuss the analysis and classification of complex alloys on the basis of sphere packing using the concept of triangulated co-ordination shells. The main properties of these co-ordination shells were discussed in an earlier paper (Frank & Kasper, 1958).

The new A_4B_3 structure is regarded by Frank & Kasper as a modification of the $CaZn_5$ structure in which the Ca atoms, which lie along the hexagonal axes of the simple kagomé net at $z = 0$, are replaced by two smaller atoms at $z = \frac{1}{4}$ and $z = \frac{3}{4}$. In the case of Zr_4Al_3 the Ca atoms are replaced by Zr atoms ($\frac{1}{3}, \frac{2}{3}, \frac{1}{4}$ and $\frac{1}{3}, \frac{2}{3}, \frac{3}{4}$). The Zn' and Zn'' atoms of the $CaZn_5$ structure are replaced by Al atoms at ($\frac{1}{3}, \frac{1}{3}, 0$) and Zr atoms at ($\frac{2}{3}, \frac{1}{3}, \frac{1}{2}$), respectively, in the Zr_4Al_3 structure. The Zr atoms in the $z = \frac{1}{4}$ and $z = \frac{3}{4}$ positions have an asymmetrical Z14 co-ordination shell which is oblate and leads to the apparent compression of the Zr atoms. According to Frank & Kasper such Z14 co-ordination shells are generally oblate and normally occupied by the atoms of transition elements. As far as is known Zr_4Al_3 is the first compound to be reported having the new structure and this would appear to add some force to the new concepts governing the structure of complex alloys enunciated by Frank & Kasper.

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