

## Crystal Structure Investigations on the Zr-Al and Hf-Al Systems

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A review is given of phase analysis and structure studies on the Zr-Al and Hf-Al systems. The structures and properties of the phases are discussed and compared with those of some transition metal borides and silicides and other metal phases.

The atomic parameters of  $\text{Hf}_2\text{Al}_3$  have been refined.

When the work on the binary systems Zr-Al and Hf-Al was began at this Institute two years ago, the structures of only two phases, *viz.*  $\text{Zr}_3\text{Al}$  and  $\text{ZrAl}_3$ , were known in the zirconium-aluminium system. No investigation at all had been reported on the hafnium-aluminium system. Recently the two systems have been extensively investigated by the present author and independently by various other investigators. The intermetallic compounds that have been crystallographically characterized are listed in Table 1.

In this paper the results of the present phase analysis are given. Some features concerning the structures are discussed and the refinement of the crystal structure of  $\text{Hf}_2\text{Al}_3$  is presented.

### I. PHASE ANALYSIS OF THE Zr-Al AND Hf-Al SYSTEMS

#### Experimental

The alloys were prepared from weighed amounts of hafnium (98.5 % from I.C.I.), zirconium (99.9 % from Foote Mineral Company) and aluminium (99.99 %) by melting in an electric arc furnace under an atmosphere of argon. No chemical analyses have been made since the melting losses were relatively small — not exceeding 1 % up to aluminium contents corresponding to the formulae of  $\text{ZrAl}_3$  and  $\text{Hf}_2\text{Al}_3$ . This implies that accurate data cannot be given for the actual compositions of various phases. The work has been concentrated on structure determinations and not on the phase diagram.

The specimens were also studied after a period of heating followed by quenching in water. The zirconium alloys were heated at 875°C and the hafnium alloys at 850°C for about 2–4 weeks. The heat treatments were carried out with pieces of the crushed alloys sealed in evacuated silica tubes. Tantalum foils protected the alloys from reacting with the silica.

Table 1. Crystallographic data of phases in the Zr-Al and Hf-Al systems. The unit axes given refer to the first reference in the reference column.

	Structure type	Lattice parameters (in Å)			Refs.
Zr <sub>3</sub> Al	<i>L1</i> <sub>2</sub>	<i>a</i> = 4.372			1
Zr <sub>2</sub> Al	<i>D8</i> <sub>3</sub>	<i>a</i> = 4.894	<i>c</i> = 5.928		2,3
Zr <sub>5</sub> Al <sub>3</sub>	<i>D8</i> <sub>m</sub>	<i>a</i> = 11.049	<i>c</i> = 5.396		4
Zr <sub>5</sub> Al <sub>3</sub> O <sub>x</sub>	ternary <i>D8</i> <sub>3</sub>	<i>a</i> = 8.177	<i>c</i> = 5.674		4
Zr <sub>3</sub> Al <sub>2</sub>	tetragonal	<i>a</i> = 7.630	<i>c</i> = 6.998		5
Zr <sub>4</sub> Al <sub>3</sub>	hexagonal	<i>a</i> = 5.433	<i>c</i> = 5.390		6
Zr <sub>2</sub> Al <sub>3</sub>	orthorhombic	<i>a</i> = 9.601	<i>b</i> = 13.906	<i>c</i> = 5.57	7,3
ZrAl <sub>3</sub>	<i>C14</i>	<i>a</i> = 5.282	<i>c</i> = 8.748		8
ZrAl <sub>3</sub>	<i>D0</i> <sub>23</sub>	<i>a</i> = 4.306	<i>c</i> = 16.90		9
Hf <sub>5</sub> Al <sub>3</sub> O <sub>x</sub>	ternary <i>D8</i> <sub>3</sub>	<i>a</i> = 8.066	<i>c</i> = 5.678		10,11
Hf <sub>3</sub> Al <sub>2</sub>	Zr <sub>3</sub> Al <sub>2</sub>	<i>a</i> = 7.535	<i>c</i> = 6.906		10,3
Hf <sub>4</sub> Al <sub>3</sub>	Zr <sub>4</sub> Al <sub>3</sub>	<i>a</i> = 5.343	<i>c</i> = 5.422		3,11
HfAl	<i>Bf</i>	<i>a</i> = 3.253	<i>b</i> = 10.831	<i>c</i> = 4.282	12
Hf <sub>2</sub> Al <sub>3</sub>	Zr <sub>2</sub> Al <sub>3</sub>	<i>a</i> = 9.523	<i>b</i> = 13.763	<i>c</i> = 5.522	13,3
HfAl <sub>2</sub>	<i>C14</i>	<i>a</i> = 5.23	<i>c</i> = 8.66		11,3,4
HfAl <sub>3</sub>	<i>D0</i> <sub>23</sub>	<i>a</i> = 3.98	<i>c</i> = 17.2		11,3,4,14
HfAl <sub>3</sub>	<i>D0</i> <sub>22</sub>	<i>a</i> = 3.93	<i>c</i> = 8.89		11,3

The identification of the samples was performed by means of the X-ray powder patterns obtained in a Guinier focusing camera using monochromatized CuK $\alpha$ <sub>1</sub> radiation and with KCl as internal standard.

## Results

*The Zr-Al system.* The zirconium-aluminium phase diagram was investigated by McPherson *et al.*<sup>15</sup> and the following intermediate phases were reported: Zr<sub>3</sub>Al below 975°C, Zr<sub>2</sub>Al below 1 250°C, Zr<sub>5</sub>Al<sub>3</sub> formed from the melt but breaking down at lower temperatures, Zr<sub>3</sub>Al<sub>2</sub> and Zr<sub>4</sub>Al<sub>3</sub> both formed from melt, ZrAl formed in the solid state and stable below 1 250°C and Zr<sub>2</sub>Al<sub>3</sub>, ZrAl<sub>2</sub>, ZrAl<sub>3</sub> all formed from melt.

The present study of the arc-melted alloys confirms the results of McPherson *et al.* However, the powder photograph of Zr<sub>4</sub>Al<sub>3</sub> was diffuse depending on incomplete equilibrium. In the tempered region, there is one exception. The existence of the binary phase ZrAl reported by McPherson *et al.* could not be confirmed but it may be that this is a ternary phase containing hafnium since HfAl seems to be very stable. Because of slow reactions, each of the powder patterns of Zr<sub>3</sub>Al, Zr<sub>2</sub>Al and Zr<sub>3</sub>Al<sub>2</sub> contained lines from their neighbouring phases.

*The Hf-Al system.* The phase diagram of the hafnium-aluminium system has so far not been described except for the aluminium end of the diagram<sup>16</sup>. The present study has revealed the existence of five binary compounds in arc-melted samples at the compositions of Hf<sub>3</sub>Al<sub>2</sub>, HfAl, Hf<sub>2</sub>Al<sub>3</sub>, HfAl<sub>2</sub> and HfAl<sub>3</sub>. The same phases, and also a phase Hf<sub>4</sub>Al<sub>3</sub>, were found in samples heated at 850°C. Compound analogous to the zirconium phases Zr<sub>3</sub>Al, Zr<sub>2</sub>Al and Zr<sub>5</sub>Al<sub>3</sub> have not been observed but the rate of reaction seems to be very low at 850°C in the hafnium-rich part of the system and therefore the phase conditions in this region merit further study.

## II. SOME FEATURES CONCERNING THE CRYSTAL CHEMISTRY OF THE INTERMEDIATE PHASES FOUND IN THE Zr-Al AND Hf-Al SYSTEMS

 Silicide-like structures:  $\text{Me}_5\text{Al}_3$ ,  $\text{Me}_3\text{Al}_2$  and  $\text{MeAl}$ .

There are many similarities in the crystal chemistry of some zirconium and hafnium-aluminides and the borides and silicides of the transition metals\*. This does not seem to be the case with other transition metal aluminides. This is probably due to the atomic sizes, Zr and Hf being considerably larger than the other transition metals and giving a metal radius ratio with aluminium that is comparable with the ratios present in borides and silicides. This assumption seems to be supported by the fact that another large metal atom, thorium, also forms boride- and silicide-like aluminides, *viz.*  $\text{Th}_3\text{Al}_2$  of the  $D5_a$  type (*e.g.*  $\text{V}_3\text{B}_{1-2}$  and  $\text{U}_3\text{Si}_2$ ),  $\text{ThAl}$  of the  $B_7$  type (*e.g.*  $\text{CrB}$  and  $\text{CaSi}$ ) and  $\text{Th}_2\text{Al}$  of the  $C16$  type (*e.g.*  $\text{Cr}_2\text{B}$  and  $\text{Ta}_2\text{Si}$ ).

$\text{Me}_5\text{Al}_3$ . Only one phase has been found with this composition, *viz.*  $\text{Zr}_5\text{Al}_3$ <sup>4</sup>.  $\text{Zr}_5\text{Al}_3$  is isomorphous with  $\text{W}_5\text{Si}_3$  of the  $D8_m$  type and the structure is built up by a zirconium-aluminium net shown in Fig. 1a. This net is repeated along the  $c$ -axis by translating it half the diagonal distance of the  $ab$  plane marked in the figure. The holes between two successive nets are filled with aluminium and zirconium (*cf.* Fig. 1b). The zirconium atoms in the holes are fourteen-coordinated and form compressed chains along the  $c$ -axis like chains in other  $D8_m$  structures. The Zr—Zr distances in these chains are 2.70 Å (normal Zr—Zr = 3.20). Wilson *et al.* described  $\text{Zr}_5\text{Al}_3$  as belonging to the  $D8_8$  structures<sup>18</sup>. In the present author's opinion, this is probably a ternary  $D8_8$  phase

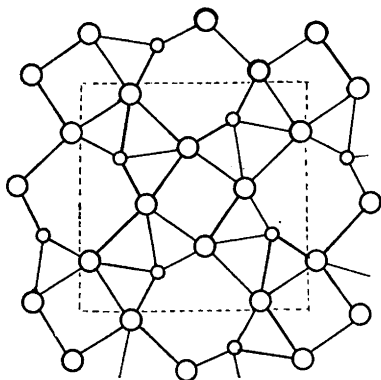


Fig. 1a. The metal atom net of  $\text{Zr}_5\text{Al}_3$  ( $D8_m$ ). Zr atoms are shown as large circles and Al atoms as small circles. The  $ab$  plane of the unit cell is indicated with dashed lines.

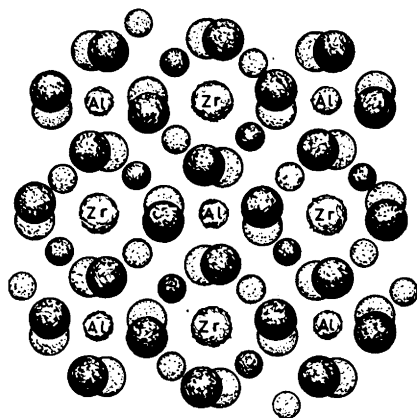


Fig. 1b. The atomic arrangement of  $\text{Zr}_5\text{Al}_3$  ( $D8_m$ ) seen along the  $c$ -axis. The lettered atoms are situated at  $z = 1/4$  between the main layers at  $z = 0$  and  $z = 1/2$ .

\* The borides and silicides of the transition metals have recently been reviewed by Aronsson<sup>17</sup>

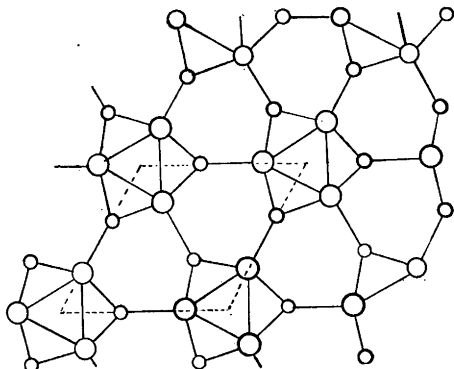


Fig. 2a. The metal atom net of  $Zr_5Al_3O_x$  ( $D8_h$ ).

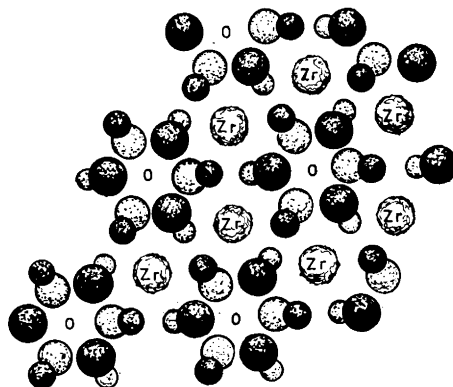


Fig. 2b. The atomic arrangement of  $Zr_5Al_3O_x$  ( $D8_h$ ) seen along the  $c$ -axis. The two main layers are at  $z = 1/4$  and  $z = 3/4$  and the latter atoms at  $z = 1/2$ . The octahedral voids in  $000$  and  $00\frac{1}{2}$  are marked with the letter  $O$ .

of the  $Me_5Si_3(X)$  type ( $X = O$ ) since a gradual addition of oxygen to the  $D8_m$  phase finally gave pure  $D8_h$ <sup>4</sup>. The ternary  $D8_h$  phases have been studied particularly by Nowotny. Aronsson has suggested that the interstitial atoms are located in the octahedral voids of the  $D8_h$  structure<sup>19</sup>. These voids are formed when the metal net seen in Fig. 2a is repeated along the  $c$ -axis by a rotation of  $60^\circ$ . The positions of the voids in the hexagonal cell are  $000$  and  $00\frac{1}{2}$  and if they are completely filled with oxygen the formula will then be  $Zr_5Al_3O$ . However, the oxygen contents have not so far been estimated and the formula is therefore written  $Zr_5Al_3O_x$ .

Though the  $D8_m$  phase is not found in the hafnium-aluminium system, the ternary phase  $Hf_5Al_3O_x$  ( $D8_h$ ) is formed when oxygen is added to samples of the approximate composition  $HfAl_{0.6}$ <sup>10</sup>.

$Me_3Al_2$ . The isotypic compounds  $Zr_3Al_2$  and  $Hf_3Al_2$  are very closely related to silicides belonging to the so-called  $CuAl_2$  family. Following Frank and Kasper<sup>20,21</sup>, structures of this type are built up by a square-triangle net  $3^2.4.3.4$  or, in Black's notation, by an A-layer<sup>22</sup>. In the  $D5_a$  type of structure represented by  $U_3Si_2$ , these A-layers are placed directly above each other. The cubic holes are filled with uranium atoms and the triangular prismatic holes with silicon.  $Zr_3Al_2$  and  $Hf_3Al_2$  are built up in the same way by two differently deformed A-layers. This arrangement (*cf.* Fig. 3) makes the  $c$ -axes of these phases twice the length of the  $c$ -axis of  $U_3Si_2$  and the aluminium atoms are translated from their ideal positions at  $z = 0.25$ .

The ratio  $r_{Me}/r_X$  calculated for the seven  $U_3Si_2$ -type structures tabled by Aronsson<sup>17</sup> are between the values 1.31 and 1.67 if the C.N. 12 radii given in the same paper are used. The ratio  $r_{Zr}/r_{Al} = r_{Hf}/r_{Al}$  should be about 1.2. The aluminium atom thus seems to be too large to fit into a regular triangular prism formed by hafnium or zirconium in an atomic arrangement of  $U_3Si_2$  type.

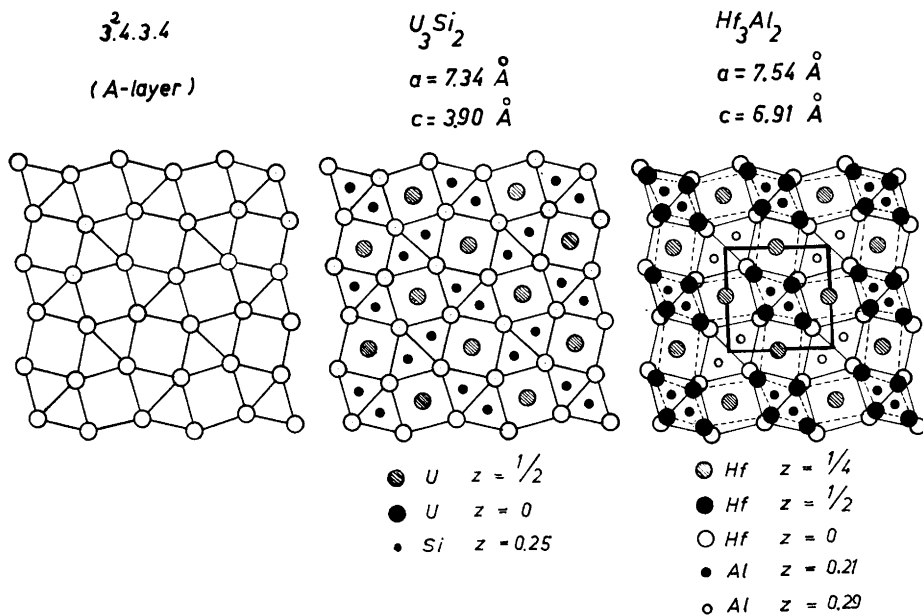


Fig. 3. The relationship between  $Hf_3Al_2$  and  $U_3Si_2$  ( $D5_a$ ).

In this connection the tetragonal phase  $Zr_3Zn_2$  reported by Petersen and Rinn<sup>23</sup> seems to be of considerable interest. A structure for this phase is not proposed by these authors but the X-ray data reported indicate that it is most probably isomorphous with  $Zr_3Al_2$  and  $Hf_3Al_2$ . Since the radius of Zn is slightly larger than that of Al, this fact will support the assumption that the size factor is important for the formation of the  $Zr_3Al_2$  type of structure.

*MeAl*. Only the compound HfAl has been found with this composition. HfAl is isomorphous with CrB. Short Al—Al distances corresponding to the short B—B distances along the zig-zag chains in CrB are not found in HfAl. According to Aronsson<sup>17</sup>, the "electronic" requirements on the smaller component may not be crucial for the stability of the  $B_7$ -type structures. This assumption is exemplified by the structure of HfAl and even more by the phase CeNi recently reported by Finney and Rosenzweig<sup>24</sup>.

#### The NiAs-family structure $Zr_2Al$ .

The  $B8_2$  structure  $Zr_2Al$  may also be included among the silicidelike phases. The  $B8_2$  structures belong to the NiAs-family. The only silicide reported with a  $B8_2$  structure is  $Ni_2Si$  but several silicides have the  $C22$  and  $C23$  type of structure which are also members of the NiAs-family. The occurrence of the  $B8_2$  and  $D8_8$  type, represented by  $Zr_2Al$  and  $Zr_5Al_3$ , belonging to the same binary system has been discussed by Wilson *et al.*<sup>2</sup> It may be observed, however that the  $D8_8$ -phase found in the zirconium-aluminium system is probably ternary.

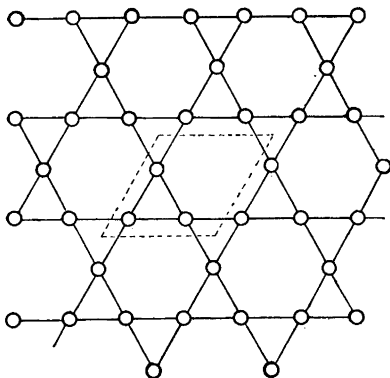


Fig. 4a. The kagomé net of aluminium in  $Zr_4Al_3$ .

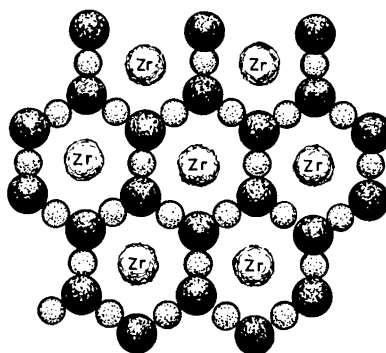


Fig. 4b. The atomic arrangement of  $Zr_4Al_3$ , seen along the  $c$ -axis. The kagomé net of aluminium is situated at  $z = 0$ , the honeycomb net of zirconium at  $z = 1/2$  and lettered atoms at  $z = 1/4$  and  $z = 3/4$ .

### The $\sigma$ -phase-like structure $Me_4Al_3$

The  $\sigma$ -like structure  $Me_4Al_3$  contains metal chains with very short Me—Me distances ( $Zr-Zr = 2.70 \text{ \AA}$ ), very much like the chains found in  $Zr_5Al_3$  of the  $D8_m$  type of structure ( $Zr-Zr = 2.70 \text{ \AA}$ ). This is in agreement with the statement by Frank and Kasper<sup>21</sup> that the distances between atoms having this type of environment (Z14 atoms) should be short. It is interesting to note that the structure of  $Zr_3Al_2$  (the composition of which is intermediate between those of the two former) contains  $Zr-Zr$  distances of normal length. This also suggests that the close metal-metal approach in  $Zr_4Al_3$  and  $Zr_5Al_3$  depends on the geometrical arrangement rather than on some kind of bonding between the metal atoms.

The similarity between the  $\sigma$ -phase and the  $Zr_4Al_3$ -type of structure was pointed out by Wilson *et al.*<sup>6</sup> The existence of  $\sigma$ -phases in the niobium and tantalum-aluminium systems, with the compositions  $Nb_2Al$ <sup>25,26</sup> and  $Ta_2Al$ <sup>27</sup>, are worth noting in this connection. The structures of  $Zr_4Al_3$  and  $Ta_2Al$  seen along the  $c$ -axis are demonstrated in Figs. 4 and 5. The large density of the Z14 atoms is the most striking resemblance between the two structure types. However, the layers that build up the structures differ considerably.  $Ta_2Al$  is built up by a kagomé-tiling net containing both tantalum and aluminium atoms. This net is repeated along half the  $c$ -axis by the translation  $a/2$  and  $b/2$  and a rotation of  $90^\circ$ .  $Zr_4Al_3$  on the other hand is built up from kagomé nets of aluminium atoms and hexagonal honeycomb layers of zirconium atoms stacked on each other along the  $c$ -axis.

As pointed out by Wilson *et al.*, the  $Zr_4Al_3$  type of structure is identical with the hypothetical "split calcium  $CaZn_5$  structure" derived by Frank and Kasper<sup>20</sup>. However, it is also interesting to observe the great similarities between  $Zr_4Al_3$  and  $\epsilon$ -TaN or also  $\delta$ -TiO<sub>x</sub> studied by Andersson and found to

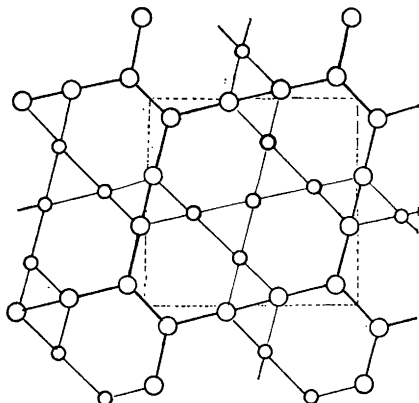


Fig. 5a. The kagomé-tiling net of  $Ta_2Al$  ( $\sigma$ -phase). Ta atoms are shown as large circles and Al atoms as small circles.

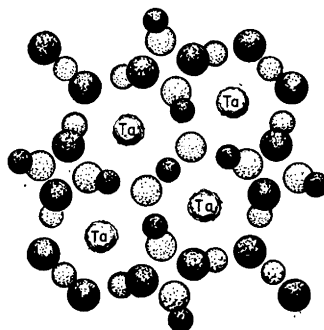


Fig. 5b. The atomic arrangement of  $Ta_2Al$  seen along the  $c$ -axis. The two kagomé nets are at  $z = 0$  and  $z = 1/2$  and the lettered Ta atoms at  $z = 1/4$  and  $3/4$ .

show about 50 % vacancies in the nonmetal positions<sup>28</sup>. The latter structure may alternatively be described as an interstitial solution of oxygen in a metal structure of the  $\omega$ -phase type. The analogies between  $CaZn_5$ ,  $Zr_4Al_3$  and  $\delta-TiO_x$  are shown in Fig. 6. All these structures may be regarded as being built up by kagomé nets and honeycomb nets. The filling-in of the tunnels formed by the hexagons of the layers is different in the three structures.

### Other structures

$Zr_3Al$  ( $L1_2$ ),  $ZrAl_2$  ( $C14$ ) and  $HfAl_2$  ( $C14$ ) belong to well-known structure families and will not be discussed here. Except for these structures and those described above, there are two other phases occurring in the two systems, viz.  $Me_2Al_3$  and  $MeAl_3$ .

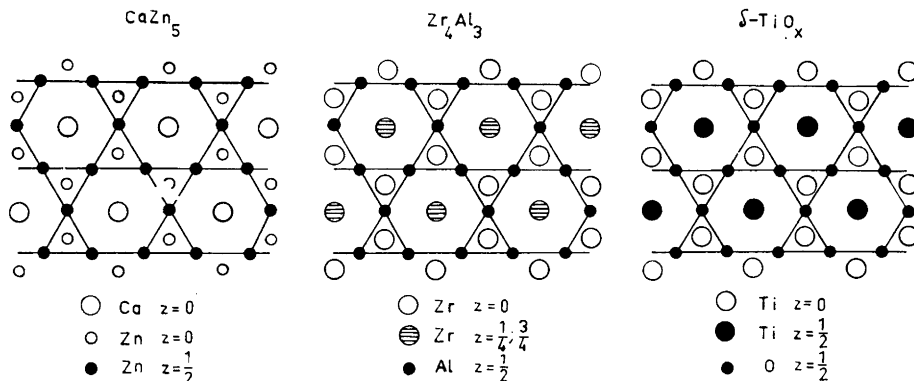


Fig. 6. The relationship between the structures of  $CaZn_5$ ,  $Zr_4Al_3$  and  $\delta-TiO_x$ .

$Me_2Al_3$ . The crystal structures of the isomorphous  $Zr_2Al_3$  and  $Hf_2Al_3$  have recently been reported<sup>3,7,13</sup>. This type of structure will be discussed in connection with the refinement of  $Hf_2Al_3$  (*v. infra*).

$MeAl_3$ .  $ZrAl_3$  is of the  $D0_{23}$  type whilst  $HfAl_3$  crystallizes in both the  $D0_{23}$  and  $D0_{22}$  forms. These two structure types have been described by Brauer<sup>9</sup> and are formed by ordered substitution of transition metals in the aluminium structure. Ti, V, Nb and Ta give a  $MeAl_3$  structure of the  $D0_{22}$  type but the larger zirconium atom results in the formation of the  $D0_{23}$  type. The fact that  $HfAl_3$  crystallizes in both the  $D0_{23}$  and  $D0_{22}$  forms has been independently reported by Schubert *et al.*<sup>3</sup> and Boller *et al.*<sup>11</sup> It is astonishing to find that the very small difference in size ( $r_{Zr} = 1.595$  kX and  $r_{Hf} = 1.585$  kX at CN 12) between Zr and Hf should cause the formation of only the  $D0_{23}$  type in the zirconium-aluminium system but both the structure types in the hafnium-aluminium system.

### III. THE CRYSTAL STRUCTURE OF $Hf_2Al_3$

#### Experimental

Very small crystals could be found in the crushed melt of  $Hf_2Al_3$ . Weissenberg photographs were taken with rotation around the  $a$ -axis and the  $c$ -axis using  $CuK$  radiation. The multiple film technique was employed and the relative intensities were visually estimated by comparison with an intensity scale.

Two and three dimensional Fourier syntheses and also structure factors were obtained using the digital electronic computer BESK with programs devised by Westman *et al.*<sup>29</sup> and Asbrin *et al.*<sup>30</sup> No corrections were made for absorption but the real part of the dispersion correction for hafnium ( $-7$ ) was taken from the table of Dauben and Templeton<sup>31</sup>.

#### Derivation of the structure

The single crystal photographs showed that  $Hf_2Al_3$  is orthorhombic. Accurate cell dimensions were obtained from Guinier powder photographs, giving the axes of the orthorhombic cell:

$$a = 9.52_3, \quad b = 13.76_3, \quad c = 5.52_2 \text{ \AA}.$$

The density of the compound was found experimentally to be  $8.00 \text{ g cm}^{-3}$ . With eight formula units  $Hf_2Al_3$  per unit cell, the theoretical density can be calculated to be  $8.04 \text{ g cm}^{-3}$ . The powder pattern of  $Hf_2Al_3$  is given in Table 2.

Reflections  $hkl$  were observed only for  $h + k = 2n$  and  $k + l = 2n$ ,  $0kl$  only for  $k + l = 4n$  and  $h0l$  only for  $l + h = 4n$ . The probable space group is thus  $Fdd2$ .

The space group contains only positions  $16(b)$  and  $8(a)$ . From space considerations (length of the  $c$ -axis only  $5.5 \text{ \AA}$ ), the 16 hafnium atoms in the unit cell must be placed in position  $16(b)$  while the remaining 24 aluminium atoms must be distributed over  $16(b)$  and  $8(a)$  positions. The Patterson projection along  $[001]$  gave approximate  $x$  and  $y$  parameters for these positions and the parameters were refined by successive calculations of the electron density projection.



Table 2. The Guinier powder pattern of  $\text{Hf}_2\text{Al}_3$  ( $\text{CuK}\alpha_1$  radiation).

<i>hkl</i>	$\sin^2\theta_{\text{obs}}$	$\sin^2\theta_{\text{calc}}$	<i>I</i> <sub>obs</sub>	<i>I</i> <sub>calc</sub>	<i>hkl</i>	$\sin^2\theta_{\text{obs}}$	$\sin^2\theta_{\text{calc}}$	<i>I</i> <sub>obs</sub>	<i>I</i> <sub>calc</sub>
111	0.0291	0.0291	st	18.9	640	0.2858	0.2856	w	2.8
220	0.0387	0.0387	st	19.7	462	—	0.2953	—	0.1
131	0.0541	0.0542	st +	29.4	282	0.3044	0.3044	w	4.1
240	0.0762	0.0763	st	18.1	480	—	0.3051	—	0.1
311	0.0815	0.0815	st +	24.5	004	0.3120	0.3113	w	4.0
022	0.0905	0.0904	st	16.4	353	—	0.3123	—	0.9
202	0.1042	{ 0.1040 }	vst	15.5	602	0.3135	0.3133	m	5.2
151		{ 0.1043 }		28.2	622	0.3260	0.3259	w	3.3
400	—	0.1047	—	0.0	391	0.3319	0.3320	m	6.0
331	0.1064	0.1065	m +	10.0	173	0.3352	0.3351	w	4.0
222	0.1165	0.1165	m +	13.2	571	0.3364	0.3365	m	8.0
420	0.1172	0.1172	m +	12.3	2.10.0	0.3393	0.3394	w	4.1
260	0.1389	0.1389	vw	2.1	513	0.3422	0.3418	m	4.8
242	—	0.1541	—	0.3	711	—	0.3431	—	0.8
440	—	0.1548	—	0.1	660	—	0.3483	—	0.4
351	0.1566	0.1566	w	2.8	224	0.3504	0.3500	w	4.7
171	0.1794	0.1795	m	6.7	642	—	0.3635	—	0.1
113	0.1845	0.1848	vw	2.3	533	0.3675	{ 0.3669 }	m	3.4
511	0.1862	0.1861	m	6.2	731		{ 0.3681 }		4.7
062	0.1907	0.1906	vw	2.1	482	0.3830	0.3829	w	2.9
422	—	0.1950	—	0.2	373	0.3877	{ 0.3875 }	m +	5.7
080	0.2002	0.2004	vw	2.8	244		{ 0.3876 }		6.9
133	0.2099	0.2098	m	6.8	0.10.2	0.3908	0.3910	m	7.8
531	0.2109	0.2112	w	4.4	1.11.1	0.4045	0.4050	vw	3.3
262	0.2167	0.2167	w	3.0	404	—	0.4160	—	0.1
460	0.2174	0.2174	m	5.7	553	—	0.4170	—	2.0
280	0.2266	0.2266	vw	1.0	2.10.2	—	0.4172	—	0.2
371	0.2318	0.2318	m	5.7	4.10.2	—	0.4179	—	0.1
442	0.2326	0.2326	st	16.8	751	0.4183	{ 0.4183 }	m +	7.6
313	0.2375	0.2371	m	4.8	800		{ 0.4187 }		4.4
620	0.2480	0.2480	w	3.6	662	0.4263	0.4261	vw	3.7
153	0.2601	0.2600	m	8.1	424	0.4290	0.4285	m	8.8
551	0.2613	0.2613	vw	1.7					
333	0.2625	0.2622	w	3.0					
191	0.2795	0.2797	vw	1.6					

The Patterson projection along [100] shows that the 16 Hf and 16 Al are all situated in planes perpendicular to the *c*-axis and with a spacing of about 0.25*c*. The *z*-parameter of the aluminium atom in 8(*a*) could also be estimated in this Patterson projection. However, the relatively low scattering power of the aluminium atom makes the accuracy of the aluminium position rather low.

The resulting parameters are:

$$16 \text{ Hf in } 16(b) : x = 0.185, \quad y = 0.054, \quad z = 0.00$$

$$16 \text{ Al in } 16(b) : x = 0.185, \quad y = 0.129, \quad z = 0.50$$

$$8 \text{ Al in } 8(a) : x = 0, \quad y = 0, \quad z = 0.63$$

Interatomic distances are given in Table 3. The final *R*-values were 10.8 % for the *hk0*, 12.1 % for the *hkl*, 14.5 % for the *hk2*, 12.9 % for the *hk3* and 13.1 % for the *0kl* reflections. No temperature factor was applied.

Table 3. Interatomic distances in  $\text{Hf}_2\text{Al}_3$ .

Hf 2 Hf	3.37 Å	Al(a) 2 Hf	2.80 Å	Al(b) 1 Hf	2.81 Å
2 Hf	3.38	2 Hf	2.85	1 Hf	2.90
1 Al(a)	2.80	2 Hf	3.17	1 Hf	2.90
1 Al(a)	2.85	2 Al(b)	2.60	2 Hf	2.95
1 Al(a)	3.17	2 Al(b)	2.75	1 Hf	3.00
1 Al(b)	2.81			1 Al(a)	2.60
1 Al(b)	2.90			1 Al(a)	2.75
1 Al(b)	2.90			2 Al(b)	2.75
2 Al(b)	2.95				
1 Al(b)	3.00				

The crystal structure of  $\text{Zr}_2\text{Al}_3$ , which is isomorphous with  $\text{Hf}_2\text{Al}_3$ , has been given by both Renouf and Beever<sup>7</sup> and Schubert *et al.*<sup>3</sup> The  $z$ -parameters of the aluminium atoms in 16(b) differ in the two investigations, *viz.* 0.500 as reported by Renouf and Beever and 0.45 by Schubert *et al.* The former value seems to be preferred for packing reasons and is in close agreement with the one found for  $\text{Hf}_2\text{Al}_3$  in this study ( $z = 0.49$  from a three-dimensional Fourier synthesis within a "box" around this position<sup>29</sup>). The aluminium atoms in the special position were found to have the  $z$  co-ordinate 0.63 by three-dimensional calculations and this is in accordance with the value found in the Patterson projection along [100].

### The structure

The structure of  $\text{Zr}_2\text{Al}_3$  and  $\text{Hf}_2\text{Al}_3$  has been described by Renouf and Beever as being built up by puckered triangular nets<sup>7</sup>. These nets, containing as many zirconium atoms as aluminium atoms, are repeated along the  $y$  axis and leave holes that are filled with aluminium atoms. It is interesting to note that a plane-packing of equal numbers of zirconium or hafnium atoms and aluminium atoms is realized by the square-triangle net of the  $3^3.4^2$  type found in  $\text{HfAl}$ <sup>12</sup> while the triangular packing of the type found in  $\text{Zr}_2\text{Al}_3$  and  $\text{Hf}_2\text{Al}_3$  reveals a departure from planarity.

In a preliminary note, the structure was described in terms of  $\text{Hf}_2\text{Al}_3$  units. Each such unit forms a triangular bipyramid with Hf atoms in the tops and three Al atoms in the corners of the pyramids. This description is a rather formal one since two of the aluminium atoms are not in contact with each other in the pyramid. Similar pyramids with close-packed arrangements of atoms are found in the hexagonal  $\text{HfAl}_2$  of the  $C14$  type.

Attempts to find simple relationships between  $\text{Hf}_2\text{Al}_3$  and other alloy structures were unsuccessful and it is remarkable that  $\text{A}_2\text{B}_3$ -phases with a ratio  $r_A/r_B$  of about 1.2 seem to be very rare.

The author wishes to thank Professor A. Magnéli for his encouraging interest and many valuable comments. Thanks are also due to Dr. S. Andersson who introduced me to this field of chemistry.

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Received June 9, 1961.