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# The Crystal Structure of HfAl

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The crystal structure of HfAl is of the $B_f$ (CrB) structure type. The orthorhombic unit cell, space-group *Cmcm* (No. 63), has the dimensions $a = 3.25_3$ Å, $b = 10.83_1$ Å and $c = 4.28_2$ Å. A comparison between HfAl and other $B_f$ structures is given.

Studies on arc-melted hafnium-aluminium alloys by means of X-ray powder methods have revealed the existence of the phases $Hf_3Al_2$, HfAl, $Hf_2Al_3$, $HfAl_2$ and $HfAl_3$. The structure types of $Hf_3Al_2$, $HfAl_2$ and $HfAl_3$ were reported in a previous note [1,2]. In the course of further studies on this system the crystal structure of HfAl has been derived.

## EXPERIMENTAL

The alloy was prepared by arc-melting an equimolecular mixture of hafnium metal (98.5 % from I.C.I) and high-purity aluminium in an argon atmosphere. Crystals of HfAl were obtained by crushing the melt. They formed thin plates that could be cut down to dimensions suitable for single-crystal studies. A complete set of data was registered in a Weissenberg camera using Cu$K$ radiation and rotating the crystal around an axis situated in the plane of the crystal ($a$ axis). The intensities of the reflexions were estimated visually.

Accurate unit cell dimensions were obtained from photographs taken in a Guinier focusing camera using stirctly monochromatized Cu$Ka_1$ radiation and applying a procedure described in a previous communication from this Institute [3].

## DERIVATION OF THE STRUCTURE

The single crystal data obtained showed the structure to be orthorhombic. The unit cell dimensions derived from the Guinier powder photograph were:

$$a = 3.25_3 \text{ Å}, \qquad b = 10.83_1 \text{ Å}, \qquad c = 4.28_2 \text{ Å}.$$

The observed density of 8.97 indicated that the unit cell contains 4 formula units of HfAl, the calculated density being 9.07. The powder pattern of HfAl is given in Table 1.

*Table 1.* The Guinier powder pattern of HfAl ($CuK\alpha_1$ radiation)

| *hkl* | $\sin^2\Theta_{obs}$ | $\sin^2\Theta_{calc}$ | $I_{obs}$ | $I_{calc}$ |
|---|---|---|---|---|
| 020 | 0.02021 | 0.02023 | m | 7.0 |
| 021 | 0.05257 | 0.05259 | vst | 24.4 |
| 110 | 0.06109 | 0.06111 | mw | 4.8 |
| 040 | 0.08091 | 0.08091 | w | 3.1 |
| 111 | 0.09351 | 0.09347 | vvst | 30.3 |
| 130 | 0.10150 | 0.10156 | st | 16.9 |
| 041 | 0.11324 | 0.11327 | st | 12.6 |
| 002 | 0.12945 | 0.12944 | m | 7.5 |
| 131 | 0.13398 | 0.13392 | vvw | 0.6 |
| 022 | 0.14970 | 0.14967 | vw | 1.6 |
| 060 | 0.1823 | 0.18205 | m | 3.0 |
| 150 | | 0.18248 | | 2.4 |
| 112 | 0.19056 | 0.19055 | w | 2.2 |
| 042 | 0.21040 | 0.21035 | w | 2.1 |
| 061 | — | 0.21441 | — | 0.1 |
| 151 | 0.21486 | 0.21484 | m | 7.9 |
| 200 | 0.22418 | 0.22420 | w | 3.8 |
| 132 | 0.23101 | 0.23100 | st | 12.2 |
| 220 | 0.24444 | 0.24444 | vw | 0.9 |
| 221 | 0.27673 | 0.27679 | mw | 5.7 |
| 170 | 0.30400 | 0.30384 | w | 2.2 |
| 240 | 0.30504 | 0.30511 | vw | 1.5 |
| 023 | 0.3115 | 0.31147 | mst | 2.6 |
| 062 | | 0.31149 | | 3.4 |
| 152 | | 0.31192 | | 2.7 |
| 080 | 0.32358 | 0.32365 | vvw | 0.6 |
| 171 | 0.3370 | 0.33620 | mw | 5.7 |
| 241 | | 0.33747 | m | 8.3 |
| 113 | 0.3530 | 0.35235 | mw | 7.3 |
| 202 | | 0.35364 | mw | 5.5 |
| 081 | 0.35606 | 0.35601 | w | 4.1 |
| 043 | 0.37209 | 0.37215 | w | 4.1 |
| 133 | — | 0.39280 | — | 0.2 |
| 260 | 0.40626 | 0.40625 | w | 3.4 |
| 172 | 0.4335 | 0.43328 | m | 4.5 |
| 242 | | 0.43455 | | 3.1 |
| 082 | 0.45322 | 0.45309 | vw | 1.4 |
| 190 | 0.46557 | 0.46567 | mw | 4.5 |
| 063 | 0.4735 | 0.47329 | mw | 0.1 |
| 153 | | 0.47372 | | 7.0 |

Reflexions *hkl* were observed only for $h + k = 2n$, $0kl$ for $k = 2n$, $h0l$ for $h = 2n$ and $l = 2n$ and $hk0$ for $h + k = 2n$. The probable space-groups thus are *Cmcm* (No. 63), $Cmc2_1$ (No. 36) and *Ama*2 (No. 40). The symmetry, the unit-cell dimensions and the appearance of the Patterson projection along [100] suggested that the phase is isomorphous with CrB. Both the hafnium and aluminium atoms are thus in the point positions 4(*c*) of the space-group *Cmcm*:

$$\pm (0,\ y,\ \tfrac{1}{4}); \qquad \pm (\tfrac{1}{2},\tfrac{1}{2} + y,\ \tfrac{1}{4})$$

Approximate values of the $y$ parameters were obtained from the Patterson projection and the signs of the $F(0kl)$ could be calculated. The projection of

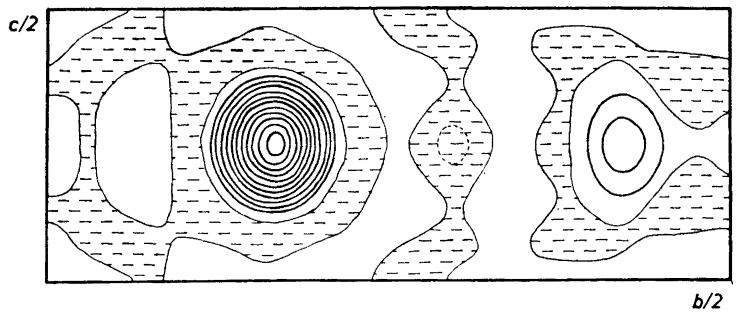


*Fig. 1.* a). Projection along [100] of the electron density of HfAl.

the electron density along [100] thus calculated (*cf.* Fig. 1a) gave the following parameter values:

$$y_{Hf} = 0.167 \qquad y_{Al} = 0.42_5$$

The difference synthesis $\varrho\ (F(0kl)_{obs} - F(0kl)_{Hf})$ gave the same value for the $y_{Al}$ parameter (*cf.* Fig. 1b). However, the accuracy of the aluminium position is rather low due to the relatively low scattering power of this atom. The index of agreement

$$\Sigma\,||\,F(0kl)_{obs}\,| - |\,F(0kl)_{calc}\,||\,/\,\Sigma\,|\,F(0kl)_{obs}\,|$$

corresponding to this structure is 0.11. Table 1 gives a comparsion between calculated and observed powder intensity data. The interatomic distances are given in Table 2.

## DISCUSSION

Following Frank and Kasper [4], the structure of HfAl can be described as a $3^3 \cdot 4^2$ tessilation in the $z = \frac{1}{4}$-plane. This tessilation repated by the $2_1$ axes parallel to [001] is demonstrated in Fig. 2. It is interesting to note that the zig-zag aluminium chains thus formed (A—B in Fig. 2) have quite normal

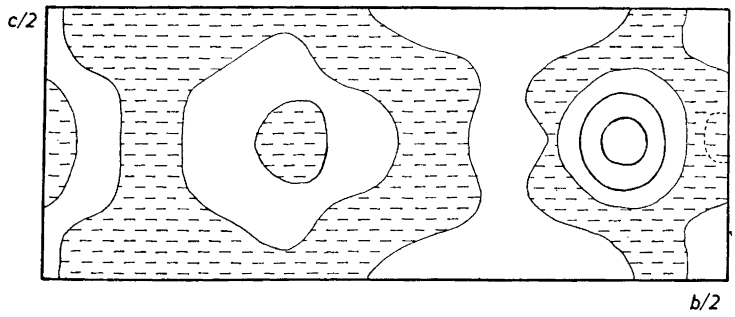


*Fig. 1.* b). The difference synthesis $\varrho\ (F(0kl)_{obs} - F(0kl)_{Hf})$. Shadowed areas indicate negative values.

*Table 2.* Interatomic distances in HfAl.

| | | | | | |
|---|---|---|---|---|---|
| Hf | 4 Hf | 3.26 Å | Al | 4 Hf | 2.86 Å |
| | 2 Hf | 3.25 | | 2 Hf | 3.07 |
| | 4 Al | 2.86 | | 1 Hf | 2.82 |
| | 2 Al | 3.07 | | 2 Al | 3.25 |
| | 1 Al | 2.82 | | 2 Al | 2.69 |

distances of about 2.69 Å. The corresponding boron-boron distances in CrB determined by Kiessling are extremely short and are probably due to boron-boron bonds of a covalent type [5,6].

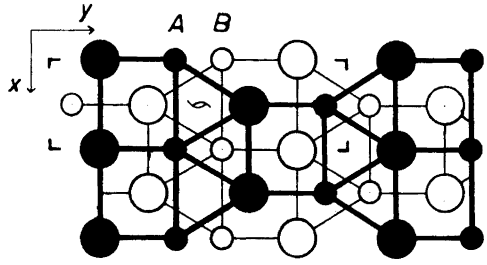


*Fig. 2.* The $3^3.4^2$ tessilation of HfAl. Large (Hf) and small (Al) black circles represent atoms at $z = \frac{1}{4}$ and open ones atoms at $z = \frac{3}{4}$. The unit cell is indicated by ⌊_.

The isomorphism between HfAl and ThAl (described by Braun [7] on a different system of axes) is also of considerable interest since the aluminium-aluminium distances along the zig-zag chains of the latter phase are reported to be as short as 2.46 Å. It might be that this is a matter of the relative size of the atoms, the ratios $r_{Th}/r_{Al}$ and $r_{Cr}/r_B$ being approximately the same and substantially higher than $r_{Hf}/r_{Al}$. However, the analogous crystal structure of ThCo does not support this assumption [8] since the cobalt-cobalt distances are 2.77 Å in spite of the atomic radius of cobalt being less than that of aluminium.

The atomic distances within the chains of several other phases of $B_f$ structure, uncluding CaSi[9], CaGe [10], CaSn [10] and YSi [11], are throughout of the long "normal" type.

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