ACTA CHEMICA SCANDINAVICA 22 (1968) 2191–2199

The Crystal Structure of Hf_3P_2

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The crystal structure of Hf_3P_2 has been determined using single-crystal methods. The space group is *Pnma*. The cell dimensions are:

$$a = 10.138 \text{ Å}; \; b = 3.578 \text{ Å}; \; c = 9.881 \text{ Å}$$

The unit cell contains 12 hafnium and 8 phosphorus atoms, all situated in 4(c) positions.

The structure can be described as a complex arrangement of PHf_6 triangular prisms. The phosphorus atoms coordinate 7 or 8 hafnium atoms, while the hafnium atoms have coordination numbers of 14, 15, or 16. The refinement, yielding a discrepancy index of 7.9 % after the application of absorption and extinction corrections, has given Hf—Hf distances with standard deviations of 0.001—0.002 Å and Hf—P distances with standard deviations of 0.007 Å.

The structure of Hf_3P_2 is closely related to that of Cr_3C_2 and may be considered as the anti-type of the Sb_2S_3 structure.

In a previous paper on the Hf—P system [1] the existence of a phase with the approximate composition Hf_3P_2 was reported. Further work on this phase has now confirmed the composition Hf_3P_2 and a structure determination and refinement is described in the present paper.

EXPERIMENTAL

Preparation. An alloy with the nominal composition $HfP_{0.75}$ was prepared by reacting turnings from zone-refined polycrystalline bars of hafnium, containing 3 % zirconium (from Koch-Light, claimed non-metallic impurity content less than 10 ppm H_2, 10 ppm C, 10 ppm N_2, and 50 ppm O_2) and red phosphorus of better than 99 % purity in evacuated silica capsules at 850°C. The product was then arc-melted in an atmosphere of purified argon. A needle-like single-crystal from this melt, which also contained traces of HfP, was used for collecting the intensity data.

X-Ray work. The powder sample was investigated using a Guinier-Hägg type focussing camera with strictly monochromatic Cr$K\alpha_1$ radiation (λ (Cr$K\alpha_1$) = 2.28962 Å) and with silicon as internal calibration standard (a = 5.43054 Å).

The intensity data were recorded by rotating the crystal about the b axis, in a Weissenberg camera using Zr-filtered Mo$K\alpha$ radiation. The multiple film technique with iron foils as absorbers between successive films was used. The intensities were estimated visually with an intensity scale obtained from one of the reflections of the same crystal.

The crystal used was fairly well-formed with the approximate dimensions $0.120 \times 0.032 \times 0.018$ mm (0.120 mm along the rotation axis). An absorption correction was applied using eight limiting planes of the forms {101} and {100} and a linear absorption coefficient of 800 cm^{-1}.

UNIT CELL DATA

The characteristics of the unit cell were as follows:

Orthorhombic Hf_3P_2
$a = 10.138$ Å; $b = 3.578$ Å; $c = 9.881$ Å
$D_{calc} = 11.1$ g/cm³
Number of formula units in the unit cell $Z=4$.
Systematic absences:

$hk0$ absent when $h = 2n + 1$
$0kl$ absent when $k + l = 2n + 1$

Possible space groups: $Pnma$ or $Pn2_1a$

The lattice parameters given above were measured on the arc-melted specimen from which the single-crystal was picked. They are in good agreement with those reported [1] for the two-phase-region Hf_3P_2—HfP at 1000°C:

$a=10.140$ Å, $b=3.577$ Å; $c=9.883$ Å;

The accuracy is estimated to be higher than 0.04 %. X-Ray powder data for Hf_3P_2 are presented in Table 1. No experimental determination of the density

Table 1. Powder diffraction data for Hf_3P_2 as measured with a Guinier-Hägg camera using Cr$K\alpha_1$ radiation.

$h\ k\ l$	$\sin^2\theta_{obs} \times 10^4$	$\sin^2\theta_{calc} \times 10^4$	$p \cdot \lvert F_{calc}\rvert^2 \times 10^{-4}$	I_{obs}
2 0 1	644.0	644.0	3.1	w
1 0 2	664.0	664.2	1.5	vw
2 0 2	1046.9	1046.6	6.5	w
3 0 1	1284.5	1281.3	11.1	st
1 1 1		1285.7	45.8	
2 1 0	1532.6	1533.9	1.1	vw
2 1 1	1668.6	1668.1	79.3	vst
3 0 2	1684.9	1683.9	63.6	st
2 0 3	1717.7	1717.5	2.1	vw
2 1 2	2070.1	2070.7	54.8	st
4 0 1	2173.4	2173.6	45.6	st
0 1 3	2230.6	2231.7	112.4	vst
1 0 4	2273.9	2274.4	54.7	st
3 1 1	2305.1	2305.4	49.5	st
1 1 3	2358.8	2359.2	34.1	m
4 0 2	2577.2	2576.1	34.8	m
2 0 4	2657.7	2656.8	36.9	m
3 1 2	2708.5	2708.0	99.7	st
4 1 1	3197.2	3197.7	28.4	m
1 1 4	3297.0	3298.5	18.7	w
5 0 1	3319.8	3320.7	22.9	w
4 1 2	3601.2	3600.2	24.5	w
2 0 5	3865.2	3864.4	33.8	m
0 0 2	4097.1	4096.4	95.1	st

was undertaken. It would have been unreliable on account of the unknown porosity of the sample. However, an estimation of the density from the known values for Hf_2P and HfP showed that the cell content should be $Hf_{12}P_8$ or $Hf_{12}P_9$, of which the first alternative proved to be correct.

SOLUTION OF THE STRUCTURE

The diffraction symmetry showed that only *Pnma* and $Pn2_1a$ were possible as space groups. Position 8(*d*) in space group *Pnma* was excluded from space considerations (the *b* axis is only 3.577 Å). Furthermore a comparison of the Weissenberg films showed that the ratio $F_o(hkl)/F_o(hk+2l)$ was constant within experimental errors. This strongly suggests that the atomic positions are limited to two planes, situated at a distance of 0.5 *b* from each other and perpendicular to the *b*-axis. For this reason positions 4(*a*) and 4(*b*) in *Pnma* were also excluded. The choice was thus limited to position 4(*c*) in the centrosymmetric *Pnma* and position 4(*a*) in the non-centrosymmetric $Pn2_1a$.

The two Patterson sections $P(u,0,w)$ and $P(u,1/2,w)$ were calculated using intensities from the *h*0*l* and *h*1*l* Weissenberg films. These calculations as well as all further calculations mentioned in this paper were performed on the Control Data (CD 3600) computer in Uppsala using programs listed in Table 2. By analyzing the Harker vectors in these sections a reasonable arrangement of hafnium atoms was found. Furthermore, with the phosphorus atoms located from space considerations all hafnium-phosphorus vectors ended on positive regions of the Patterson function. An electron density section $(x,0,z)$ was then calculated without introducing the phosphorus contributions when calculating the signs. In this section the phosphorus atoms appeared at the expected positions as well as the hafnium atoms. This was considered as strongly indicating that the correct structure had been found.

The refinement of the structure was performed with a full-matrix least-squares program (No. 4 in Table 2), using 283 *h*0*l* and 291 *h*1*l* reflexions. After

Table 2. Computer programs used for the crystallographic calculations on the CD 3600 computer in Uppsala (all programs written in FORTRAN IV).

Program performing	Authors
1. Least squares refinement of unit cell dimensions.	J. Tegenfeldt, Uppsala, Sweden.
2. Lorentz-polarization, absorption and extinction corrections.	P. Coppens, L. Leiserowitz and D. Rabinovich, Rehovoth, Israel; modified by O. Olofsson and M. Elfström, Uppsala and (incorporation of extinction correction) by B. Brandt and S. Åsbrink, Stockholm, Sweden.
3. Least squares refinement of positional parameters and temperature factors.	P. K. Gantzel, R. A. Sparks and K. N. Trueblood, Los Angeles, U.S.A.; modified by A. Zalkin, Berkeley, U.S.A. and by C.-I. Brändén, R. Liminga and J.-O. Lundgren, Uppsala, Sweden.
4. Fourier summations and structure factor calculations.	A. Zalkin, Berkeley, U.S.A.; modified by R. Liminga and J.-O. Lundgren, Uppsala, Sweden.
5. Interatomic distances.	A. Zalkin, Berkeley, U.S.A.

the first 5 refinement cycles, varying 10 positional parameters and two scale factors, the discrepancy index

$$R = \sum||F_o|-|F_c||/|F_o|$$

was 13.8 %. It was now apparent that the intensity material was severely affected by extinction, and to some extent also by absorption. Consequently an absorption correction was applied using program 2 in Table 2, followed by five refinements cycles on an intensity material from which the 60 strongest reflexions were excluded. The R-value after this calculation including refinement of the temp. factors was 8.1 %. An extinction correction was applied according to Zachariasen [2]

$$F_{o,\,corr} \approx F_o \cdot \{1 + c \cdot \beta(2\theta) \cdot I_c\}$$

The β-function used was the following (see Table 2, Program 2 and Ref. 10)

$$\beta(2\theta) = \frac{(1 + q \cdot \cos^4 2\theta) \cdot \mathrm{Lp} \cdot 2}{(1 + q \cdot \cos^2 2\theta) \cdot \sin 2\theta} \cdot \frac{\mathrm{d}A^*}{\mathrm{d}\mu}\,(2\theta),$$

where A^* denotes the absorption for the reflexion, μ the linear absorption coefficient and where q is 1 for an unpolarized incident beam. The values of c used was 1.2×10^{-3} with I_o on an absolute scale. After the application of this correction all reflexions were included in the refinement. Atomic scattering factors were taken from Ref. 3 and the real part of the anomalous dispersion correction from Ref. 4. The reflexions were weighted according to the formula

$$w = 1/(a + |F_o| + c \cdot |_o|F^2 + d \cdot |F_o|^3)$$

with $a=70.0$, $c=0.035$, and $d=0.0001$. Reflexions too weak to be observed were not included. The parameters varied in the last cycles of refinement were: 10 positional parameters, 5 isotropic temperature factors and 2 scale factors. The final R-value was 7.9 % with all 574 reflexions included, and the last shifts were less than 5 % of the calculated standard deviations for all parameters.

The positional and thermal parameters and their standard deviations are given in Table 3. The reasonable values obtained for the temperature factors indicate that the applied absorption and extinction corrections were satisfactory.

As a check on the refinement a difference-Fourier section for the asymmetric part of the unit cell was finally calculated. The largest positive or negative

Table 3. Final structure data for Hf_3P_2. Space group *Pnma*. All atoms in position 4(c) with $y=1/4$. $a=10.138$ Å, $b=3.578$ Å, and $c=9.881$ Å.

Atom	x	$\sigma(x)$	z	$\sigma(z)$	B	$\sigma(B)$
Hf(1)	0.04668	0.00010	0.12629	0.00010	0.29	0.01
Hf(2)	0.37613	0.00010	0.06439	0.00010	0.29	0.01
Hf(3)	0.21615	0.00010	0.79647	0.00010	0.29	0.01
P(1)	0.30851	0.00072	0.49890	0.00073	0.36	0.08
P(2)	0.47390	0.00077	0.82207	0.00076	0.45	0.09

Table 4. Weight analysis from the last cycle of refinement. $\Delta = ||F_o| - |F_c||$.

Interval F_o	Number of reflexions	$\overline{w \cdot \Delta^2}$ (normalized)	Interval $\sin\theta$	Number of reflexions	$\overline{w \cdot \Delta^2}$ (normalized)
0— 48	57	1.09	0.00—0.46	197	1.11
48— 57	57	0.73	0.46—0.58	102	0.69
57— 65	58	1.03	0.58—0.66	66	0.75
65— 72	57	1.07	0.66—0.73	48	0.99
72— 81	58	0.83	0.73—0.79	39	0.86
81— 98	57	1.06	0.79—0.84	34	0.67
98—114	57	0.81	0.84—0.88	25	0.86
114—149	58	0.82	0.88—0.92	25	0.97
149—194	57	1.22	0.92—0.96	24	1.33
194—618	58	1.34	0.96—0.99	14	1.77

regions of this difference map were evenly distributed and less than 15 % of the phosphorus peaks of the F_o-synthesis. No sign of anisotropic thermal vibrations or residual extinction were discernible in the difference synthesis.

An analysis of the weighting used in the last cycle of refinement is shown in Table 4. There is a comparison of the (absorption and extinction corrected) observed and calculated structure factors in Table 5.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Interatomic distances are given in Table 6. The table includes all distances smaller than 4.25 Å.

The following features of the structure are apparent from Fig. 1, which shows the atomic arrangement as viewed along the b-axis. The two phosphorus

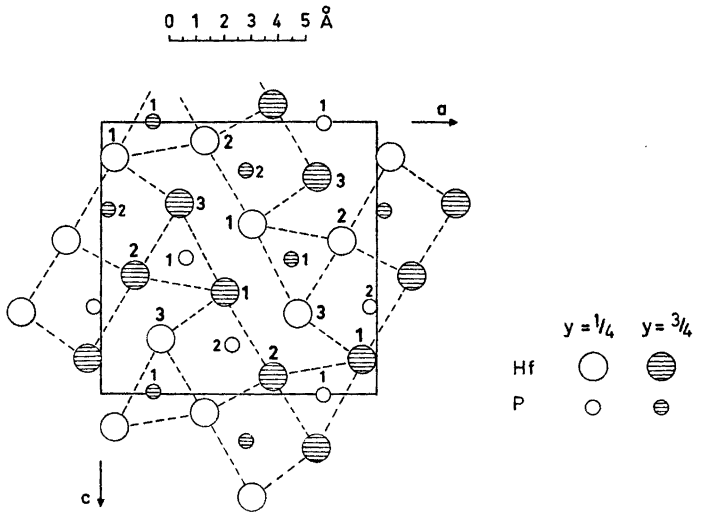

Fig. 1. The crystal structure of Hf_3P_2.

Table 5. Observed and calculated structure factors. The observed structure factors are corrected for absorption and extinction.

h	k	l	$\|F_o\|$	$\|F_c\|$
0	0	4	95.7	120.1
0	0	6	47.9	41.4
0	0	8	104.9	114.9
0	0	10	66.8	69.6
0	0	12	195.1	194.1
0	0	14	146.4	166.9
0	0	16	213.1	204.2
0	0	22	82.7	89.5
0	0	26	38.7	39.6
1	0	2	48.2	60.3
1	0	3	162.4	211.0
1	0	4	344.6	369.8
1	0	5	38.0	41.7
1	0	6	172.4	160.1
1	0	7	232.9	231.7
1	0	8	102.1	108.6
1	0	9	270.3	244.9
1	0	10	64.4	68.2
1	0	11	72.8	85.8
1	0	12	150.3	139.9
1	0	13	99.3	116.5
1	0	16	74.9	76.0
1	0	18	132.0	137.0
1	0	23	74.5	76.7
1	0	25	60.2	66.4
1	0	26	58.1	57.6
2	0	1	73.2	88.7
2	0	2	102.6	127.3
2	0	4	344.9	303.6
2	0	5	329.6	290.6
2	0	7	165.5	147.4
2	0	8	219.7	199.8
2	0	9	205.7	191.0
2	0	10	148.0	154.3
2	0	11	130.2	120.2
2	0	13	104.6	92.2
2	0	14	73.9	73.7
2	0	16	71.6	79.3
2	0	20	129.4	128.5
2	0	21	87.0	110.9
2	0	22	63.7	62.4
3	0	1	155.1	166.2
3	0	2	312.8	398.7
3	0	3	50.0	52.9
3	0	5	414.8	321.8
3	0	6	99.2	88.0
3	0	7	36.7	34.2
3	0	8	102.4	103.9
3	0	9	86.2	79.4
3	0	10	62.9	65.4
3	0	11	131.8	132.0
3	0	12	65.9	68.8
3	0	14	203.1	197.1
3	0	15	54.1	54.5
3	0	16	97.9	102.0
3	0	17	107.9	112.6
3	0	18	51.8	51.0
3	0	19	65.7	62.3
3	0	20	68.8	65.9
3	0	21	49.5	50.8
3	0	25	35.1	33.7
3	0	26	37.5	40.5
4	0	1	288.1	337.6
4	0	2	254.1	295.1
4	0	5	139.1	131.9
4	0	6	180.3	188.0
4	0	8	142.3	132.5
4	0	10	195.2	177.7
4	0	11	193.6	176.9
4	0	12	130.8	127.4
4	0	13	118.0	135.1
4	0	14	52.8	51.2
4	0	15	38.3	36.9
4	0	16	60.2	50.6
4	0	17	69.6	79.6
4	0	18	61.6	71.2
5	0	1	197.5	239.1
5	0	3	42.5	44.1
5	0	5	108.9	102.3
5	0	6	435.7	343.8
5	0	7	224.0	204.4
5	0	8	74.9	66.0
5	0	10	219.3	209.0
5	0	15	199.2	174.3
5	0	19	69.8	58.1
5	0	20	68.3	67.4
5	0	22	72.0	78.3
5	0	23	52.4	51.9
6	0	0	56.6	66.3
6	0	1	56.4	60.2
6	0	2	51.3	50.8
6	0	3	476.2	418.8
6	0	4	31.5	28.2
6	0	6	29.4	25.5
6	0	7	106.8	103.4
6	0	9	158.7	141.3
6	0	11	151.5	164.3
6	0	12	80.8	69.1
6	0	13	92.1	81.7
6	0	15	113.9	116.7
6	0	17	91.7	90.8
6	0	19	148.9	165.5
6	0	21	61.3	64.3
7	0	1	234.5	251.3
7	0	2	46.2	50.1
7	0	3	151.3	150.6
7	0	4	129.0	121.3
7	0	5	91.7	86.9
7	0	6	226.5	214.7
7	0	7	181.7	163.7
7	0	10	202.0	203.9
7	0	12	63.3	63.1
7	0	13	53.2	51.3
7	0	14	54.8	52.2
7	0	15	162.6	184.2
7	0	20	59.2	52.3
7	0	22	75.3	67.2
7	0	26	65.8	68.4
8	0	1	284.6	281.3
8	0	2	88.3	105.9
8	0	4	68.7	69.3
8	0	5	73.8	72.4
8	0	6	142.6	140.1
8	0	8	232.1	243.6
8	0	9	56.3	56.3
8	0	10	91.7	101.3
8	0	11	143.3	154.7
8	0	12	92.3	89.9
8	0	13	111.5	127.3
8	0	17	71.1	67.4
8	0	22	55.4	51.9
8	0	23	59.4	63.2
8	0	24	73.1	87.5
8	0	25	40.1	48.7
9	0	1	170.8	172.3
9	0	2	166.8	162.1
9	0	4	61.8	75.3
9	0	5	271.4	266.8
9	0	6	37.2	31.7
9	0	7	113.3	108.4
9	0	8	50.4	43.4
9	0	9	67.2	65.3
9	0	11	98.2	97.8
9	0	12	76.3	69.6
9	0	14	99.7	103.0
9	0	15	57.4	47.3
9	0	17	152.7	157.6
9	0	19	79.3	78.9
9	0	20	53.3	46.9
9	0	21	50.3	45.6
9	0	25	37.5	38.2
10	0	0	42.0	37.2
10	0	1	114.1	136.8
10	0	2	37.2	33.5
10	0	4	186.0	188.2
10	0	5	156.3	171.1
10	0	7	85.0	85.2
10	0	8	162.0	154.2
10	0	9	169.8	149.7
10	0	10	81.2	74.9
10	0	12	63.2	60.0
10	0	13	137.5	139.3
10	0	16	67.5	63.0
10	0	20	99.6	90.9
10	0	21	104.0	105.5
11	0	3	235.8	216.3
11	0	4	197.6	205.6
11	0	7	66.4	71.7
11	0	10	74.6	73.8
11	0	11	77.2	68.6
11	0	12	106.8	103.4
11	0	13	147.1	133.5
11	0	23	54.4	50.0
12	0	0	391.3	373.3
12	0	1	51.2	47.3
12	0	3	87.8	91.7
12	0	4	68.4	76.5
12	0	6	54.5	53.7
12	0	7	69.4	68.1
12	0	8	72.0	70.2
12	0	9	83.8	84.1
12	0	12	146.5	133.2
12	0	14	113.1	112.1
12	0	16	156.6	137.8
12	0	22	63.1	70.9
13	0	2	71.6	80.7
13	0	3	37.2	37.6
13	0	4	179.4	156.4
13	0	5	55.6	52.6
13	0	6	119.7	116.9
13	0	7	208.6	190.2
13	0	8	74.8	72.2
13	0	9	138.4	118.8
13	0	12	79.4	80.2
13	0	16	67.2	54.9
13	0	18	124.6	123.1
13	0	19	59.2	48.7
13	0	23	57.5	71.1
14	0	2	90.5	99.0
14	0	3	48.4	49.6
14	0	4	113.9	99.4
14	0	5	143.2	149.8
14	0	7	93.2	88.3
14	0	8	116.6	108.8
14	0	9	89.4	93.2
14	0	10	106.5	88.2
14	0	11	135.3	141.3
14	0	20	79.1	76.2
14	0	21	64.8	60.2
14	0	22	43.7	48.7
14	0	23	29.3	32.8
15	0	1	67.9	65.6
15	0	2	215.8	221.8
15	0	5	75.2	70.7
15	0	8	65.0	63.2
15	0	10	41.0	39.2
15	0	14	152.0	153.0
15	0	15	57.7	50.4
15	0	16	76.2	74.8
15	0	18	45.9	43.8
15	0	20	62.9	49.2
16	0	1	92.5	83.2
16	0	2	153.0	164.5
16	0	5	78.4	70.5
16	0	6	79.6	81.2
16	0	7	65.7	56.3
16	0	10	137.9	114.5
16	0	11	81.3	77.6
16	0	12	81.4	80.3
16	0	13	72.8	64.1
16	0	18	58.7	59.0
16	0	20	48.3	43.0
17	0	1	59.5	56.0
17	0	6	208.3	186.4
17	0	8	68.2	62.6
17	0	10	95.7	90.0
17	0	15	67.0	61.4
17	0	18	63.8	62.0
17	0	20	50.6	50.6
18	0	0	100.8	100.3
18	0	2	57.6	51.7
18	0	3	141.8	159.7
18	0	9	59.7	52.5
18	0	11	72.6	69.8
18	0	12	93.1	91.0
18	0	13	69.7	62.3
18	0	19	79.0	87.5
19	0	3	80.8	88.0
19	0	4	104.9	106.4
19	0	10	83.7	91.4
19	0	12	56.3	56.8
19	0	15	97.6	95.5
20	0	1	96.5	88.8
20	0	4	81.6	67.6
20	0	8	151.6	153.3
20	0	11	62.3	59.1
20	0	13	70.2	62.2
21	0	1	103.1	89.9
21	0	4	59.2	55.9
21	0	5	124.5	116.4
21	0	7	67.2	59.4
21	0	11	52.7	46.2
21	0	15	41.0	33.4
21	0	17	88.7	101.4
21	0	18	34.3	32.6
22	0	1	101.1	89.8
22	0	5	57.4	54.7
22	0	8	77.8	69.2
22	0	12	57.3	52.9
22	0	13	86.3	87.0
23	0	3	107.5	102.9
23	0	4	64.4	60.2
23	0	9	78.7	73.5
23	0	10	47.2	53.2
23	0	13	72.4	70.7
24	0	0	101.9	105.6
24	0	3	84.2	66.6
24	0	9	60.9	61.5
24	0	12	51.0	46.4
26	0	5	53.7	66.6
26	0	10	31.1	30.3
27	0	2	101.7	92.3
28	0	2	65.0	60.9
0	1	3	540.6	530.0
0	1	5	33.3	34.0
0	1	7	172.3	172.9
0	1	9	194.3	193.8
0	1	11	196.3	169.6
0	1	13	114.4	111.6
0	1	15	109.0	102.0
0	1	17	95.7	95.7
0	1	19	180.1	168.8
0	1	21	62.1	56.5
1	1	3	183.7	206.5
1	1	4	129.9	152.8
1	1	5	63.7	67.3
1	1	6	258.3	295.5
1	1	7	258.2	261.4
1	1	8	57.8	59.4
1	1	10	168.2	188.4
1	1	11	65.0	61.6
1	1	12	81.4	81.5
1	1	26	51.1	57.6
1	1	27	38.4	55.3
1	1	14	36.3	37.8
1	1	15	168.9	169.0
1	1	18	56.7	52.1
1	1	20	79.3	67.4
1	1	22	72.5	82.0
1	1	23	54.9	53.2
2	1	2	211.6	261.8
2	1	4	83.4	93.9
2	1	5	81.7	80.0
2	1	6	121.7	129.8
2	1	7	47.6	51.8
2	1	8	195.1	195.1
2	1	10	129.1	121.5
2	1	11	177.2	192.7
2	1	12	151.6	149.8
2	1	13	158.2	174.5
2	1	14	70.7	60.4
2	1	16	55.0	52.7
2	1	17	76.5	74.6
2	1	18	77.3	74.7
2	1	23	67.1	74.9
2	1	24	81.1	89.2
2	1	25	51.4	53.1
3	1	1	230.9	248.9
3	1	2	278.7	352.9
3	1	3	67.3	66.5
3	1	5	300.1	289.7
3	1	6	89.3	83.0
3	1	7	102.4	115.8
3	1	8	69.8	63.1
3	1	9	86.4	76.5
3	1	11	99.2	89.8
3	1	14	157.0	160.6
3	1	15	60.5	57.7
3	1	16	64.2	63.8
3	1	17	184.3	166.9
3	1	18	65.4	62.6
3	1	19	76.7	75.2
4	1	0	42.7	45.5
4	1	1	171.9	188.5
4	1	2	167.5	174.9
4	1	7	147.9	164.2
4	1	3	45.5	44.9
4	1	4	155.5	200.5
4	1	5	200.4	218.1
4	1	8	256.1	267.8
4	1	9	221.3	207.4
4	1	10	96.6	88.0
4	1	11	67.2	75.3
4	1	13	118.1	107.8
4	1	16	88.9	90.8
4	1	20	94.2	94.5
4	1	21	113.2	105.8
4	1	22	58.2	57.7
5	1	1	63.4	63.0
5	1	2	49.6	48.7
5	1	3	245.5	272.8
5	1	4	238.5	266.0
5	1	5	50.1	43.3
5	1	6	63.6	72.8
5	1	7	174.5	160.5
5	1	8	99.7	94.4
5	1	9	176.2	202.9
5	1	10	110.6	100.6
5	1	11	58.8	49.7
5	1	12	114.6	111.0
5	1	13	146.8	138.7
5	1	16	76.2	68.9
5	1	18	114.0	119.8
5	1	23	77.9	73.8
6	1	0	617.1	512.8
6	1	2	30.1	32.7
6	1	3	62.5	61.2
6	1	4	129.0	133.4
6	1	5	36.6	32.7
6	1	6	135.0	128.0
6	1	7	31.6	24.3
6	1	8	101.8	100.1
6	1	9	47.3	43.1
6	1	12	196.2	218.6
6	1	14	160.0	146.7
6	1	16	144.5	150.9
6	1	22	92.8	101.7
6	1	26	34.1	39.5
7	1	1	33.8	28.5
7	1	2	57.1	61.3
7	1	3	193.6	193.7
7	1	4	341.4	273.4
7	1	5	62.1	61.5
7	1	6	170.2	157.6
7	1	7	186.4	190.5
7	1	8	102.7	91.4
7	1	9	131.7	122.8
7	1	11	67.3	57.2
7	1	12	135.6	120.4
7	1	13	114.0	109.5
7	1	16	69.9	63.8
7	1	18	131.6	135.1
7	1	19	76.1	73.2
7	1	23	74.6	76.4
8	1	0	60.8	58.2
8	1	2	170.0	162.8
8	1	3	59.0	60.6
8	1	4	169.2	162.2
8	1	5	211.6	219.4
8	1	6	39.2	43.1
8	1	7	104.9	108.5
8	1	8	204.6	199.4
8	1	9	144.6	138.8
8	1	10	137.1	125.1
8	1	11	159.5	143.8
8	1	13	54.2	45.5
8	1	16	70.4	62.2
8	1	20	90.9	93.0
8	1	21	85.9	87.7
8	1	22	54.3	54.0
8	1	25	42.7	51.1
9	1	1	186.2	169.2
9	1	2	302.8	297.5
9	1	3	29.3	22.3
9	1	5	99.0	94.7
9	1	6	77.9	73.9
9	1	9	47.3	47.5
9	1	12	53.5	50.9
9	1	15	66.2	65.6
9	1	16	92.3	95.5
9	1	17	107.0	103.9
9	1	20	71.5	60.6
10	1	1	192.3	169.7
10	1	2	168.1	175.5
10	1	3	42.9	38.1
10	1	4	46.1	40.8
10	1	5	104.4	96.9
10	1	6	124.3	111.0
10	1	7	55.0	55.9
10	1	8	99.9	98.5
10	1	10	160.9	159.9
10	1	11	150.8	124.5
10	1	12	117.1	112.2
10	1	13	107.6	104.1
10	1	16	71.1	62.0
10	1	18	76.6	65.8
10	1	20	59.5	55.8
10	1	23	53.5	50.4
10	1	24	71.1	82.6
11	1	1	121.5	109.7
11	1	3	57.9	60.7
11	1	5	56.4	54.5
11	1	6	251.8	258.2
11	1	7	162.2	176.2
11	1	8	69.4	73.6
11	1	9	69.0	63.5
11	1	10	137.9	134.0
11	1	15	99.7	93.4
11	1	16	57.9	54.7
11	1	18	68.3	68.8
11	1	20	71.4	63.7
11	1	22	73.7	70.9
11	1	23	52.8	51.3
11	1	24	36.1	37.0
12	1	0	174.5	166.3
12	1	2	42.4	43.4
12	1	3	269.7	262.5
12	1	7	80.7	82.8
12	1	9	92.3	100.3
12	1	10	62.5	60.5
12	1	11	103.6	109.5
12	1	12	56.9	58.5
12	1	13	82.8	79.9
12	1	15	67.7	75.6
12	1	17	69.5	72.2
12	1	19	146.5	124.3
12	1	24	28.0	32.5
13	1	1	161.2	147.3
13	1	2	61.2	57.8
13	1	4	133.1	136.7
13	1	6	98.9	95.4
13	1	7	97.1	100.6
13	1	9	44.0	39.0
13	1	10	128.9	129.7
13	1	11	65.9	59.3
13	1	12	79.1	73.7
13	1	13	58.7	45.8
13	1	14	59.0	46.1
13	1	15	156.9	146.2
13	1	21	48.9	42.9
13	1	22	57.5	51.4
13	1	23	31.7	24.6
14	1	0	47.1	40.6
14	1	1	148.1	143.6
14	1	2	90.7	84.4
14	1	4	114.1	106.0
14	1	6	73.6	73.2
14	1	8	155.8	160.9
14	1	12	68.0	68.8
14	1	13	104.5	104.2
14	1	14	80.5	72.7
14	1	23	42.8	51.0
15	1	1	91.6	97.6
15	1	2	93.6	89.1
15	1	5	205.1	208.3
15	1	7	74.8	69.0
15	1	11	84.0	92.1
15	1	17	111.8	118.4
15	1	19	62.1	69.0
15	1	21	42.3	42.5
16	1	0	81.0	72.0
16	1	1	150.0	135.0
16	1	4	95.5	97.6
16	1	5	88.0	85.9
16	1	7	80.8	75.1
16	1	8	110.3	107.3
16	1	9	112.0	111.7
16	1	12	53.8	48.6
16	1	13	103.5	102.1
16	1	16	53.2	56.0
16	1	20	51.9	55.2
16	1	21	65.1	74.2
17	1	3	127.3	123.9
17	1	4	107.8	95.0
17	1	5	56.7	51.1
17	1	7	58.0	52.0
17	1	9	121.9	133.7
17	1	10	80.8	79.9
17	1	12	58.5	56.3
17	1	13	78.5	85.7
17	1	15	65.8	65.5
18	1	0	182.9	211.3
18	1	3	82.2	78.2
18	1	4	57.8	48.5
18	1	9	72.9	67.0
18	1	12	70.5	78.3
18	1	14	76.6	74.8
18	1	15	46.5	38.9
18	1	16	83.9	96.1
19	1	2	58.7	51.5
19	1	4	110.3	106.1
19	1	5	68.4	59.7
19	1	6	84.6	85.2
19	1	7	113.7	120.2
19	1	12	64.2	61.6
19	1	19	43.5	48.6
20	1	1	69.0	56.6
20	1	2	68.8	53.0
20	1	4	68.6	60.6
20	1	5	104.6	109.0
20	1	8	58.1	50.8
20	1	10	69.1	66.2
20	1	11	101.8	114.1
21	1	1	48.3	49.1
21	1	2	127.9	135.1
21	1	14	92.2	108.0
21	1	16	50.6	58.7
22	1	1	47.3	43.2
22	1	2	82.9	85.0
22	1	10	80.3	89.7
22	1	16	41.8	45.9
23	1	6	113.1	124.4
23	1	7	59.7	64.4
23	1	9	48.2	45.9
24	1	0	104.9	102.9
24	1	3	79.7	87.9
24	1	12	60.4	61.2
25	1	1	68.2	68.[illegible]
25	1	4	73.8	75.2
25	1	10	53.2	59.0
26	1	1	49.1	44.8
26	1	8	89.7	99.8
27	1	1	43.6	46.8
27	1	4	40.3	44.5

Table 6. Interatomic distances and standard deviations for Hf_3P_2 (in Ångström units). Distances less than 4.25 Å are listed.

Atom	Dist.	St. dev.	Atom	Dist.	St. dev.
Hf(1)—2 P(1)	2.634	0.005	Hf(3)— Hf(2)	3.105	0.001
—2 P(2)	2.643	0.006	—2 Hf(1)	3.299	0.001
— P(1)	2.713	0.007	—2 Hf(1)	3.437	0.001
—2 Hf(1)	3.213	0.002	—2 Hf(3)	3.578	0.000
—2 Hf(3)	3.299	0.001	— Hf(1)	3.684	0.001
— Hf(2)	3.396	0.002			
—2 Hf(3)	3.437	0.001	P(1) —2 Hf(1)	2.634	0.005
— Hf(2)	3.512	0.001	—2 Hf(2)	2.669	0.005
—2 Hf(1)	3.578	0.000	—2 Hf(3)	2.695	0.005
— Hf(3)	3.684	0.001	— Hf(1)	2.713	0.007
			— Hf(3)	3.086	0.007
Hf(2)— P(2)	2.591	0.008	—2 P(1)	3.578	0.000
—2 P(2)	2.602	0.006	— P(2)	3.607	0.010
—2 P(1)	2.669	0.005	—2 P(2)	3.801	0.009
—2 Hf(3)	3.055	0.001	— P(2)	3.826	0.011
— Hf(3)	3.105	0.001			
—2 Hf(2)	3.336	0.002	P(2) — Hf(2)	2.591	0.008
— Hf(1)	3.396	0.002	—2 Hf(2)	2.602	0.006
— Hf(1)	3.512	0.001	— Hf(3)	2.625	0.008
—2 Hf(2)	3.578	0.000	—2 Hf(1)	2.643	0.006
			— Hf(3)	2.721	0.008
Hf(3)— P(2)	2.625	0.008	—2 P(2)	3.578	0.000
—2 P(1)	2.695	0.005	— P(1)	3.607	0.010
— P(2)	2.721	0.008	—2 P(1)	3.801	0.009
—2 Hf(2)	3.055	0.001	— P(1)	3.826	0.011
— P(1)	3.086	0.007	—2 P(2)	3.981	0.013

atoms coordinate hafnium atoms, arranged at the corners of triangular prisms with one or two further hafnium atoms situated outside the rectangular faces of these prisms. This is a very common arrangement in metal-rich phosphides.[5] The hafnium atoms of the P(1) prism lie within 2.63—2.70 Å, which is close to the sum of the 12-coordinated Goldschmidt atomic radius of Hf, 1.58 Å, and the tetrahedral covalent radius of P, 1.10 Å. The two hafnium atoms outside the quadrilateral faces are situated at 2.71 Å and 3.09 Å, indicating a fairly small interaction between the phosphorus atom and its eighth neighbour. The six hafnium prism atoms about the P(2) atom are at an average distance of 2.62 Å, and are thus closer to the central atom than the radius sum. The distance between the seventh hafnium atom and the phosphorus atom, 2.72 Å, is close to the radius sum.

The linkage of the prisms (Fig. 1) results in shortest P—P distances of 3.58 Å and thus there is no direct interaction between phosphorus atoms. The prisms are arranged in such a way that one type of prisms have their prism axis parallel to the [010] direction, the other type of prism having its prism axis in the (010) planes. The packing results in very high coordination numbers for the metal atoms, the hafnium atoms being surrounded by 5 phosphorus neighbours (in one case at as large a distance as 3.09 Å) and 9—11 hafnium atoms. The average Hf—Hf distance (from 12 non-equivalent distances in Table 6) is 3.38 Å, which is 0.2 Å larger than the radius sum of 3.16 Å.

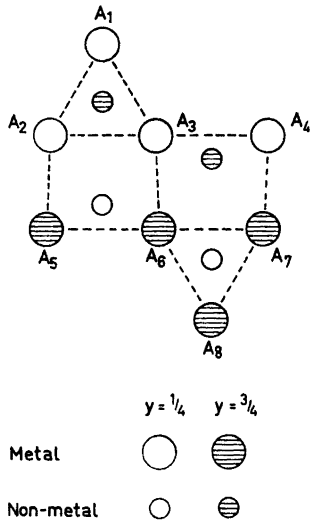

Fig. 2. Arrangement of triangular prisms found in Hf_3P_2 as well as in Cr_3C_2.

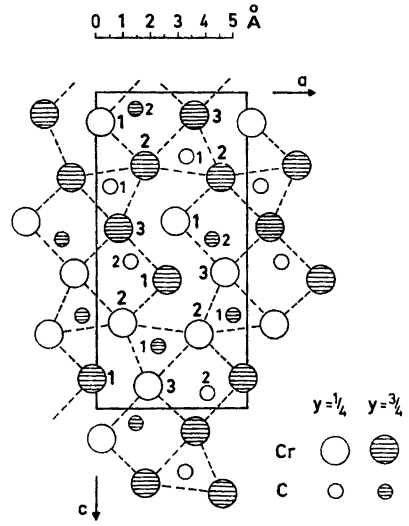

Fig. 3. The crystal structure of Cr_3C_2.

A way of describing the Hf_3P_2 structure is in terms of a group of two P(1) prisms and two P(2) prisms sharing faces as shown in the projection of Fig. 2. This description is particularly profitable when comparing the structure of Hf_3P_2 with that of Cr_3C_2. These two structures crystallize in the same space group, *Pnma*, with the same number of formula units in the unit cell and with the atoms positioned in the two mirror planes perpendicular to the short *b*-axis. A drawing of Cr_3C_2 based on the chromium positions of Hellbom and Westgren [6] and the carbon positions of Meinhardt and Krisement [7] is found in Fig. 3.

The building blocks of Fig. 2 are centered at the midpoints of the unit cell boundaries of Hf_3P_2 and linked together through sharing an edge. The atoms of the type A_1 in one building block are at the same time of the type A_4 in an adjacent building block. In Cr_3C_2 the same building blocks are found but the linkage is somewhat different. Atoms of the type A_1 in one building block are here simultaneously of the type A_2 in a neighbouring block. Thus while the structures are not isotypic they are very closely related. Although the Cr_3C_2 structure has not yet been very accurately determined, it appears that there is a tendency towards a lower coordination about the carbon atoms as compared with the phosphorus atoms in Hf_3P_2. This should be expected from space reasons since the radius ratio $r_C/r_{Cr}=0.60$ is smaller than $r_P/r_{Hf}=0.70$.

The Hf_3P_2 structure may be said to be the anti-type of the Sb_2S_3 structure.[8] The sulfur parameters are in fair agreement with the hafnium parameters, but the antimony positions differ considerably from those of the phosphorus atoms. The structures of Th_2S_3, U_2S_3, and Np_2S_3 are also of the Sb_2S_3 structure type.[9]

Acknowledgements. The author wishes to thank Prof. Gunnar Hägg for all facilities put at my disposal and for his stimulating interest. I am also indebted to Dr. Stig Rundqvist for valuable discussions.

The author is also indebted to Miss A.-C. Nordlund for her very careful work in measuring the intensities.

This work has been supported by the *Swedish Natural Science Research Council.*

REFERENCES

1. Lundström, T. and Tansuriwongs, P. *Acta Chem. Scand.* **22** (1968) 704.
2. Zachariasen, W. H. *Acta Cryst.* **16** (1963) 1139.
3. *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. III.
4. Cromer, D. T. *Acta Cryst.* **16** (1965) 17.
5. Aronsson, B., Lundström, T. and Rundqvist, S. *Borides, Silicides and Phosphides*, Methuen, London 1965.
6. Hellbom, K. and Westgren, A. *Svensk Kem. Tidskr.* **45** (1933) 141.
7. Meinhardt, D. and Krisement, O. *Z. Naturforsch.* **15a** (1960) 880.
8. Hofmann, W. *Z. Krist.* **86** (1933) 225.
9. Zachariasen, W. H. *Acta Cryst.* **2** (1949) 291.
10. Åsbrink, S. and Norrby, L. *Submitted for publication in Acta Cryst.*

Received March 1, 1968.