Table 1. Atomic coordinates, in fractions of corresponding cell edges.

	x	z
S_1	0.1470	0.0695
S_2	−0.0150	0.0865
C_1	0.1635	0.1365
C_2	−0.0135	0.1550
N_1	0.0760	0.1750
N_2	−0.1060	0.1885
O	0.2585	0.1450

$\beta = 95\ 1/2°$. Preliminary results of a complete crystal structure determination of rhodan hydrate are given here.

The space group of rhodan hydrate was found to be either $C2/c$ or C/c. The morphology of the crystals indicates [5] the presence of a twofold axis and thus the correctness of the centrosymmetric space group. The "average test" and "zero moment test" [6] also indicated centrosymmetry.

Attempts to solve the structure from Patterson projections did not succeed, and the solution was then sought by means of Harker Kasper inequalities and the "multiplication rule" [7]. This led to three possible sets of signs for the 35 strongest reflections in the b-axis projection. The molecule was recognised in one of the corresponding Fourier maps, and after three Fourier-refinements the reliability factor R was 0.115. The electron density map is reproduced in Fig. 1. The map shows that the cyclic form of rhodan hydrate, anticipated by Söderbäck [3], is correct. Further refinement will be carried out by means of $(F_o - F_c)$-technique.

1. Foss, O. and Tjomsland, O. *Acta Chem. Scand.* **12** (1958) 1799.
2. Kehl, W. L. and Jeffrey, G. A. *Acta Cryst.* **11** (1958) 813.
3. Söderbäck, E. *Ann.* **419** (1919) 217.
4. Söderbäck, E. *Ann.* **465** (1928) 184.
5. Foss, O. *Acta Chem. Scand.* **10** (1956) 868.
6. *International Tables for X-Ray Crystallography.* The Kynoch Press, Birmingham, England, 1959, Vol. II, p. 356.
7. Zachariasen, W. H. *Acta Cryst.* **5** (1952) 68.

Received June 1, 1960.

The σ-Phase Ta_2Al

LARS-ERIK EDSHAMMAR and BO HOLMBERG

Institute of Inorganic and Physical Chemistry, University of Stockholm, Stockholm, Sweden

In the course of a study of the tantalum-aluminium system recently started at this Institute, the existens of a σ-type phase has been observed in samples of the approximate composition Ta_2Al prepared by arc-melting in an argon atmosphere.

The dimensions of the tetragonal unit cell obtained from a Guinier powder pattern were found to be:

$a = 9.828$ Å $\qquad c = 5.232$ Å

The axial ratio $c/a = 0.532$ is similar to that found for other σ-phases such as the one occurring in the nickel-vanadium system studied by Kasper and Waterstrat [1] using neutron diffraction techniques. Since the ratios of the atomic radii r_{Ta}/r_{Al} and r_V/r_{Ni} are comparable, the atomic distribution reported for the nickel-vanadinium phase was tentatively adopted for Ta_2Al:

Space-group: $D_{4h}^{14}-P4/mnm$.

Unit cell content: 10 Ta_2Al.

Table 1. The Guinier powder pattern of Ta_2Al ($CuK\alpha_1$ radiation).

hkl	$\sin^2\Theta_{obs}$	$\sin^2\Theta_{calc}$	I_{obs}	I_{calc}
110	0.01228	0.01228	vw	0.5
200	—	0.02457	—	0.0
101	0.02782	0.02781	st	5.5
210	0.03068	0.03071	st *	2.5
111	0.03396	0.03396	w	2.0
220	0.04911	0.04914	vw	0.8
211	0.05238	0.05238	vw	0.8
310	0.06142	0.06142	vw	1.0
221	—	0.07081	—	0.0
301	0.07696	0.07695	w	2.2
320	0.07982	0.07985	vw	1.1
311	0.08311	0.08310	m	4.5
002	0.08670	0.08668	vw	0.7
400	0.09831	0.09828	vw	1.5
112	0.09898	0.09897	vw	1.3
321	0.10153	0.10152	vvw	0.6
410	0.10443	0.10442	vst	10.7
330	0.11059	0.11057	st	5.8
202	0.11130	0.11125	st	6.8
212	0.11739	0.11739	vst	10.0
420	0.12285	0.12285	vvw	0.5
411	0.12603	0.12609	vst	9.5
331	0.13224	0.13224	m	4.0

* Line overlaps line of neighbouring phase.

(I) 2 Al in 2(*b*).
(II) 4 Ta in 4(*f*) with $x=0.103$.
(III) 8 Ta in 8(*i*) with $x=0.371$, $y=0.037$.
(IV) 8 Al in 8(*i*) with $x=0.566$, $y=0.240$.
(V) 8 Ta in 8(*j*) with $x=0.316$, $z=0.250$.

The powder diffraction pattern required by this atomic arrangement was found to be in satisfactory agreement with the observed data (*cf.* Table 1) which evidently shows that the $\sigma(Ta_2Al)$ phase is essentially ordered.

The existence of a σ-phase in the niobium-aluminium system was recently reported by McKinsey and Faulring [2]. The composition (Nb_2Al) and powder diffraction data suggest that this phase is analogous in structure to Ta_2Al.

Further studies on the tantalum-aluminium system are in progress.

The authors wish to express their sincere gratitude to Dr. Arne Magnéli for his never-failing interest and many valuable discussions. Thanks are due to Mr. A. Eriksson for his skilful experimental assistance.

1. Kasper, J. S. and Waterstrat, R. M. *Acta Cryst.* **9** (1956) 289.
2. McKinsey, C. R. and Faulring, G. M. *Acta Cryst.* **12** (1959) 701.

Received June 21, 1960.

The Crystal Structures of Hf_3Al_2 and of $Hf_5Al_3O_x$

LARS-ERIK EDSHAMMAR

Institute of Inorganic and Physical Chemistry, University of Stockholm, Stockholm, Sweden

The existence of the phases Hf_3Al_2, $HfAl_2$, and $HfAl_3$ in the hafnium-aluminium system was reported in a previous note [1] which also gave the structure types of the two latter phases. Further studies on this system carried out on specimens obtained by arc-melting in an argon atmosphere followed by quenching to room temperature has revealed the existence of two further phases having the compositions Hf_3Al_2 and HfAl.

It was also observed that samples of compositions $HfAl_{0.5-0.7}$ gave a few very weak extra lines which could not be attributed to any of the phases mentioned above but were found to be greatly reminiscent of the strong reflexions [1] given by the oxygen-stabilized phase $Zr_5Al_3O_x$. The isomorphism thus suggested between the hafnium and the zirconium alloy phases was confirmed by gradually adding oxygen (as HfO_2) to the samples. Attempts to prepare a hafnium analogue of the oxygen-free phase Zr_5Al_3 of $D8_m$ type were unsuccessful.

The unit cell of Hf_3Al_2 was found to be tetragonal with the following dimensions:

$a = 7.535$ Å $\qquad c = 6.906$ Å

The powder pattern of the phase demonstrates clearly that it is isomorphous with the corresponding phase in the zirconium-aluminium system. The space group is $D_{4h}^{14}-P4_2/mnm$ and the atomic positions are the same as given by Wilson [2] for Zr_3Al_2:

8 Al in 8(*j*) with $x=\frac{1}{8}$, $z=0.21$.
4 Hf in 4(*f*) with $x=0.34$.
4 Hf in 4(*g*) with $x=0.20$.
4 Hf in 4(*d*).

The agreement between observed and calculated powder patterns is satisfactory.

The powder pattern of $Hf_5Al_3O_x$ could be indexed assuming a hexagonal unit cell with the dimensions:

$a = 8.066$ Å $\qquad c = 5.678$ Å

The following structure of $Hf_5Al_3O_x$ was derived from the powder data:

Cell content: 2 $Hf_5Al_3O_x$.

Space-group: $D_{6h}^3-P6_3/mcm$.

4 Hf in 4(*d*).
6 Hf in 6(*g*) with $x=0.23$.
6 Al in 6(*g*) with $x=0.59$.

The oxygen atoms have been neglected and no attempt was made to estimate the oxygen contents. It seems likely, however, that the oxygen atoms are located in interstitial positions 000 or $00\frac{1}{2}$ as suggested by Aronsson [3] for various $D8_8$ phases stabilized by small non-metal atoms.

The author wishes to express his gratitude to Dr. A. Magnéli for his kind encouragement and many helpful discussions.

1. Edshammar, L.-E. and Andersson, S. *Acta Chem. Scand.* **14** (1960) 223.
2. Wilson, C. G. and Spooner, F. J. *Acta Cryst.* **13** (1960) 358.
3. Aronsson, B. *Acta Chem. Scand.* **12** (1958) 31.

Received June 21, 1960.