lent their micro-preparations of plutonium and neptunium sulfides. Miss Anne Plettinger gave valuable aid by taking all the powder diffraction patterns.

References

HOFFMAN, W. (1933). Z. Krystallogr. 86, 225.
STROTZER, E. F. & ZUMBUSCH, W. (1941). Z. anorg. Chem. 247, 415.

ZACHARIASEN, W. H. (1948a). Acta Cryst. 1, 265.
ZACHARIASEN, W. H. (1948b). Acta Cryst. 1, 268.
ZACHARIASEN, W. H. (1948c). Acta Cryst. 1, 277.
ZACHARIASEN, W. H. (1948d). Acta Cryst. 1, 281.
ZACHARIASEN, W. H. (1948e). Acta Cryst. 1, 285.
ZACHARIASEN, W. H. (1949a). Acta Cryst. 2, 57.
ZACHARIASEN, W. H. (1949b). Acta Cryst. 2, 60.
ZACHARIASEN, W. H. (1949c). Acta Cryst. 2, 94.
ZACHARIASEN, W. H. (1949d). Acta Cryst. 2, 288.

Crystal Chemical Studies of the 5f-Series of Elements.
## XI. The Crystal Structure of α-UF₅ and of β-UF₅

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α-UF$_5$ is tetragonal body-centered with $a_1 = 6 \cdot 512 \pm 0 \cdot 001$, $a_3 = 4 \cdot 463 \pm 0 \cdot 001$ kX. and two stoichiometric molecules per unit cell. In the proposed structure each uranium atom is bonded to six fluorine atoms. The UF$_6$ octahedra are linked by shared corners into endless strings along the a_3 axis.

β-UF$_5$ is also tetragonal body-centered. The unit cell containing eight stoichiometric molecules has dimensions $a_1 = 11 \cdot 450 \pm 0 \cdot 002$, $a_3 = 5 \cdot 198 \pm 0 \cdot 001$ kX. A structure is proposed in which each uranium atom is bonded to seven fluorine atoms.

The interatomic distances are:

$$\alpha\text{-UF}_5, \quad \text{U--6 F} = 2 \cdot 20 \text{ A.}$$
$$\beta\text{-UF}_5, \quad \text{U--7 F} = 2 \cdot 23 \text{ A.}$$
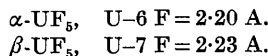
Uranium pentafluoride was first described in 1911 (Ruff & Heinzelmann, 1911). The compound was prepared in the course of war work within the Manhattan Project. P. Agron, A. Grenall, R. Kunin & S. Weller (*Manhattan Project Reports*) showed by means of X-ray diffraction patterns that uranium pentafluoride could exist in two allotropic forms. These workers did not, however, analyze the diffraction patterns. Samples of the two forms of uranium pentafluoride were submitted to me for X-ray study.

This paper deals only with crystal-structure investigation. The results of the chemical and thermodynamical studies of uranium pentafluoride will be reported elsewhere by other investigators.

The preparations of both modifications of uranium pentafluoride were microcrystalline so that only powder diffraction patterns could be obtained. The powder specimens were in sealed, thin-walled glass capillaries. All observations were made with Cu K radiation filtered through nickel foil.

1. The crystal structure of α-UF₅

Table 1 shows the X-ray diffraction data for α-UF$_5$ up to $\sin^2 \theta = 0 \cdot 400$. The observations correspond to a tetragonal body-centered translation group. The unit-cell dimensions as deduced from measurements in the back-reflection region are:

$$a_1 = 6 \cdot 512 \pm 0 \cdot 001, \quad a_3 = 4 \cdot 463 \pm 0 \cdot 001 \text{ kX.}$$

Table 1. *X-ray diffraction data for* α-UF₅

Observed intensity	$\sin^2 \theta$	$H_1 H_2 H_3$	Calculated intensity U	U and F
s	0·0282	110	17·3	16·3
m	0·0439	101	22·6	21·3
m−	0·0563	200	8·4	8·5
m	0·1000	211	15·7	9·7
m−	0·1123	220	3·4	3·7
vw	0·1195	002	1·5	3·0
s	0·1401	310	4·9	7·9
w+	0·1473	112	4·6	4·4
m−	0·1558	301	4·1	4·1
w	0·1753	202	3·5	3·6
m+	0·2118	321	5·4	5·4
w	0·2239	400	1·2	1·0
w+	0·2311	222	2·3	2·4
w	0·2515	330	1·0	0·7
m	0·2588	312	3·7	5·6
m	0·2674	411	3·5	3·3
w+	0·2800	420	1·6	2·1
w	0·2810	103	1·6	1·6
w	0·3372	213	2·5	1·8
w−	0·3420	402	1·2	1·0
w	0·3630	510	1·1	1·0
w−	0·3746	332	1·0	0·7
m−	0·3790	431, 501	3·1	2·0
vw	0·3928	303	0·9	0·9
w	0·3979	422	1·9	2·5

The volume of the unit cell (and also the observed intensities) requires two stoichiometric molecules per unit cell. The calculated density is $\rho = 5\cdot81$ g.cm.$^{-3}$.

Column 4 of Table 1 shows the intensities due to uranium atoms only, as calculated by the formula

$$I \propto |F|^2 p \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta},$$

where p is the multiplicity factor. The absorption factor has been omitted. The effect of this omission is to enhance the calculated intensities of the inner reflections relative to the outer reflections.

The a_3 period being much shorter than the a_1 period, it is to be expected that the crystallites are needle-shaped tetragonal prisms. Under the circumstances the observed intensities might very well be considerably distorted because of the high absorption and because of deviations from true randomness in the orientation of the crystallites in the specimen. A comparison between columns 1 and 4 shows a number of discrepancies. *A priori* it is, however, impossible to say to what extent the discrepancies are to be ascribed to absorption or orientation effects and to what extent to the effect of the fluorine atoms. For this reason it did not seem feasible to deduce the fluorine positions directly from the intensity observations.

Two of the ten fluorine atoms per unit cell must be in positions $(0, 0, \frac{1}{2})$, $(\frac{1}{2}, \frac{1}{2}, 0)$ if the two uranium atoms are at $(0, 0, 0)$, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Each of these fluorine atoms, the F_I atoms, is thus shared between two uranium atoms with $U-F_I = 2\cdot232$ kX. The remaining eight fluorine atoms, the F_{II} atoms, must be bonded each to one uranium atom because the U–U distances are too large to permit sharing. Hence, each uranium atom is bonded to six fluorine atoms (two F_I atoms and four F_{II} atoms). It is reasonable to assume that these six fluorine atoms form a slightly distorted octahedron about the uranium atom. The F_{II} atoms being unshared it is to be expected that the U–F_{II} distance is slightly smaller than the U–F_I distance. A value U–$F_{II} = 2\cdot18$ A. would seem reasonable. It must further be required that the distance between fluorine atoms bonded to different uranium atoms be larger than 2·6 A.

On the basis of these considerations the following structure is deduced:

Space group: $I4/m-C_{4h}^5$.
2 U atoms in $(0, 0, 0)$, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.
2 F_I atoms in $(0, 0, \frac{1}{2})$, $(\frac{1}{2}, \frac{1}{2}, 0)$.
8 F_{II} atoms in $\pm(u, v, 0)$, $(v, \bar{u}, 0)$, $(u+\frac{1}{2}, v+\frac{1}{2}, \frac{1}{2})$, $(v+\frac{1}{2}, \frac{1}{2}-u, \frac{1}{2})$,
with $u = 0\cdot315$ and $v = 0\cdot113$.

The intensities calculated from this structure are listed in the last column of Table 1. The agreement with observations is somewhat improved when the fluorine atoms are taken into account. However, there are still discrepancies. Thus the observed intensity for the reflection 002 is too low, that of the prism reflections

H_1H_10 too high. These discrepancies can be accounted for by absorption effects in long tetragonal prisms (110). It must be admitted that the observed intensities neither prove nor disprove the proposed positions for the F_{II} atoms.

Each uranium atom is bonded to six fluorine atoms forming an octahedron slightly elongated along the a_3 axis. The distances are

$$U-2 F_I = 2\cdot23 \text{ A. and } U-4 F_{II} = 2\cdot18 \text{ A.}$$

There are strings of these octahedra along the a_3 axis, each F_I atom belonging to two consecutive octahedra of a string.

The strings of octahedra are held together by van der Waals forces between fluorine atoms. The shortest F–F distances between strings of octahedra are

$$F_I-F_{II} = 2\cdot78 \text{ A. and } F_{II}-F_{II} = 2\cdot82 \text{ A.}$$

Because of the structural arrangement· one should expect the crystals to exhibit fibrous character with a_3 as the fiber axis.

The U–F bonds are probably predominantly ionic. On the assumption of ionic character of the bonds the ionic crystal radius of U^{+5} is 0·87 A.

The chemical formula of UF_5 is sometimes given as $UF_4 \cdot UF_6$, i.e. the compound is regarded as a double fluoride of tetravalent and hexavalent uranium. This view point is entirely unjustified since the uranium atoms are all equivalent in the structure.

2. The crystal structure of β-UF$_5$

The powder diffraction data for β-UF$_5$ up to $\sin^2 \theta = 0\cdot190$ are listed in Table 2. The observations correspond to a tetragonal body-centered translation group. The accurate unit-cell dimensions, as obtained from experimental data in the back-reflection region, are

$$a_1 = 11\cdot450 \pm 0\cdot002, \quad a_3 = 5\cdot198 \pm 0\cdot001 \text{ kX.}$$

The volume requirement of a fluorine atom being about 18 A.^{3} the unit cell must contain eight stoichiometric molecules. The calculated density of $\rho = 6\cdot45$ g.cm.$^{-3}$ is 10 % higher than for the alpha form.

Reflections $H_1H_2H_3$ are absent if ΣH_i is odd, and reflections $H_1H_1H_3$ are absent unless $2H_1 + H_3 = 4n$. These absences are explained if the eight uranium atoms per unit cell are placed in positions:

$$(0, 0, 0), (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) +$$
$$(x, \frac{1}{4}, \frac{1}{8}) (\bar{x}, \frac{3}{4}, \frac{1}{8}) (\frac{3}{4}, x, \frac{7}{8}) (\frac{1}{4}, \bar{x}, \frac{7}{8}),$$

corresponding to space-group symmetry $I\bar{4}2d-D_{2d}^{12}$. Good agreement between observed and calculated intensities is obtained for $x = \frac{1}{12} = 0\cdot083$. The last column of Table 2 gives the calculated values $|F|^2p$, where F is the structure factor for the uranium atoms and p the multiplicity factor.

The positions of the fluorine atoms cannot be deduced from the available diffraction data. It is, however, possible to obtain the coordinates for the fluorine atoms by means of spatial considerations.

Table 2. *X-ray diffraction data for β-UF$_5$*

$H_1H_2H_3$	$\sin^2\theta$	Observed intensity	$\lvert F\rvert^2 p$
110	—	Nil	0
200	0·0185	vw	3·1
101	0·0270	w+	17·4
220	0·0368	w−	11·3
211	0·0452	s	64·5
310	0·0457	m	48·4
301	—	Nil	0
400	—	Nil	2·5
321	0·0816	w+	29·1
330	—	Nil	0
002	—	Nil	0
420	0·0912	vw	18·9
112	0·0976	vw	18·4
411	0·0997	wm	55·3
202	0·1066	wm	41·5
510	—	Nil	0
222	—	Nil	0
312	0·1337	vvw	8·5
501, 431	0·1358	m	39·4
440	0·1456	vvw	8·3
521, 530*	0·1543	ms	87·1
402	0·1609	w	36·4
600	0·1639	w−	32·4
332	0·1701	m	64·9
620, 422	0·1818	vw	4·0
611	0·1900	w−	24·3

The following structure is proposed:

Space group $I\bar{4}2d$–D_{2d}^{12}.

Atomic positions:

$(0, 0, 0), (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})+$

8 U in $(x, \frac{1}{4}, \frac{1}{8}), (\bar{x}, \frac{3}{4}, \frac{1}{8}), (\frac{3}{4}, x, \frac{7}{8}), (\frac{1}{4}, \bar{x}, \frac{7}{8})$
with $x = 0\cdot083$.

8 F$_I$ in $(x, \frac{1}{4}, \frac{1}{8}), (\bar{x}, \frac{3}{4}, \frac{1}{8}), (\frac{3}{4}, x, \frac{7}{8}), (\frac{1}{4}, \bar{x}, \frac{7}{8})$
with $x = 0\cdot273$.

16 F$_{II}$ + 16 F$_{III}$ in

$(x, y, z), (\bar{x}, \bar{y}, z), (\bar{x}, \frac{1}{2}+y, \frac{1}{4}-z), (x, \frac{1}{2}-y, \frac{1}{4}-z),$
$(\bar{y}, x, \bar{z}), (y, \bar{x}, \bar{z}), (\bar{y}, \frac{1}{2}-x, \frac{1}{4}+z), (y, \frac{1}{2}+x, \frac{1}{4}+z)$

with parameter values as follows

	x	y	z
F$_{II}$	0·15	0·07	0·05
F$_{III}$	0·05	0·14	0·46

In the proposed structure each uranium atom is bonded to seven fluorine atoms with the following interatomic distances:

U–1 F$_I$=2·18,   U–2 F$_{II}$=2·23,   U–2 F$_{II}$=2·29

and   U–2 F$_{III}$=2·18 A.

The mean distance is U–7 F=2·23 A. Four of the seven corners of the fluorine polyhedron about uranium are shared with adjacent polyhedra.

The shortest F–F distances are

F$_I$–F$_I$=2·66,   F$_{II}$–F$_{II}$=2·92,   F$_{III}$–F$_{III}$=2·44,

F$_I$–F$_{II}$=2·52,   F$_I$–F$_{III}$=2·54,   F$_{II}$–F$_{III}$=2·55 A.

Writing the formula as UF$_4$.UF$_6$ is not justifiable since the uranium atoms are equivalent.

The results of this article were first given in *Manhattan Project Reports* in October 1943 (α-UF$_5$) and January 1946 (β-UF$_5$).

The sample of α-UF$_5$ was kindly furnished by Dr Ralph Livingston, the sample of β-UF$_5$ by Prof. W. F. Libby. The X-ray diffraction patterns of α-UF$_5$ were taken by Mr J. M. Bradford, of β-UF$_5$ by Miss Anne Plettinger.

Reference

RUFF, O. & HEINZELMANN, H. (1911). *Z. anorg. Chem.* **72**, 64.

Eindimensionale Fehlordnung in Kristallen und ihr Einfluss auf die Röntgeninterferenzen. III. Vergleich der Berechnungen mit experimentellen Ergebnissen

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Some experimental results are here compared with calculations previously communicated. Wurtzite crystals from Thrace show a high degree of disorder which cannot have arisen from transformation of parts of the crystal into zincblende. The rhombohedral modification of carbon seems to be the more stable one at low temperatures. Rotation photographs of SiC (II) crystals show a low degree of disorder and the general course of the diffuse scattering resembles that of a slightly disordered crystal of the SiC (III) type.

Einführung

In den beiden vorhergehenden Teilen dieser Arbeit— im folgenden mit I und II bezeichnet—wurden einige Berechnungen der Röntgenintensitäten eindimensional fehlgeordneter Kristalle ausgeführt. Es wurde gezeigt, dass die exakte Lösung der Problemstellung (Ermitt-