of Th_I atoms per unit cell is 0·82. The separation between consecutive Th_I atoms along the same sixfold axis is then either 4·00 or 6·00 A., the latter value occurring to the extent of 54 %.

Discussion of the structure

The figure shows the structure of Th_7S_{12} viewed along the sixfold axis. Two of the four Th_I atoms contained in the figure are shown to be at $(0, 0, \frac{1}{4})$, the other two to be at $(0, 0, \frac{3}{4})$.

Each Th_I atom is bonded to nine atoms S_{II}, while each Th_{II} atom is bonded to five S_I atoms and to three S_{II} atoms.

$a_1 = 11\cdot041\ kX.$

○ Th at $z=\frac{1}{4}$ ◕ Th at $z=\frac{3}{4}$ ◯ S at $z=\frac{1}{4}$ ◕ S at $z=\frac{3}{4}$
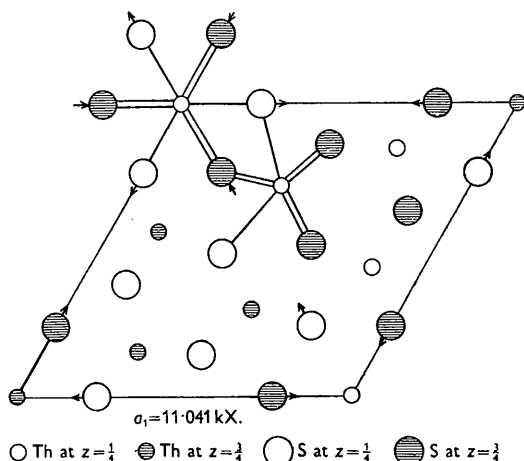
The Th_7S_{12} structure viewed along a sixfold axis. Two of the four Th_I atoms shown in the figure are placed at $z=\frac{1}{4}$ and two at $z=\frac{3}{4}$. Arrows indicate displacements of S_{II} atoms from their mean sites.

Since a Th_I atom is either at $(0, 0, \frac{1}{4})$ or at $(0, 0, \frac{3}{4})$ it becomes necessary to regard the parameters for the S_{II} atoms as variable. Consider the S_{II} atom at $(x, y, \frac{1}{4})$ with mean parameter values $x = 0\cdot235$, $y = 0$. If a Th_I

atom occupies the site $(0, 0, \frac{1}{4})$, the distance from this thorium atom to the S_{II} atom at $(x, y, \frac{1}{4})$ assumes the unreasonably small value of Th_I–$S_{II} = 2\cdot60$ A. On the other hand, one finds an unreasonably large value of Th_I–$S_{II} = 3\cdot27$ A. if the Th_I atom occupies the site $(0, 0, \frac{3}{4})$. Accordingly one may expect the S_{II} atoms to be shifted from their mean positions, the direction of the shift depending upon whether the Th_I atom occupies the site $(0, 0, \frac{1}{4})$ or the site $(0, 0, \frac{3}{4})$. The directions of the displacements of the S_{II} atoms from their mean positions are indicated by arrows in the figure.

The suggested changes in the S_{II} parameters are shown below:

$(0, 0, \frac{1}{4})$	$(0, 0, \frac{3}{4})$	x	y	Interatomic distances
Occupied	Vacant	0·255	0	Th_I–3$S_{II} = 2\cdot82$ A.
Vacant	Occupied	0·215	0	Th_I–6$S_{II} = 3\cdot09$ A.
	Mean	0·235	0	Th_I–3$S_{II} = 2\cdot60$ A.
				Th_I–6$S_{II} = 3\cdot27$ A.

The configuration of sulfur atoms about the thorium atoms is:

Th_I–3$S_{II} = 2\cdot82$ A.	Th_{II}–2$S_I\ = 2\cdot95$ A.
Th_I–6$S_{II} = 3\cdot09$ A.	Th_{II}–3$S_I\ = 2\cdot98$ A.
	Th_{II}–2$S_{II} = 2\cdot85$ A.
	Th_{II}–1$S_{II} = 3\cdot00$ A.
Mean Th_I–9$S_{II} = 3\cdot00$ A.	Th_{II}–8S $= 2\cdot94$ A.

The observed interatomic distances Th–S in thorium sulfides are:

ThS	Th–6S = 2·83 A.
Th_2S_3	Th–7S = 2·90 A.
Th_7S_{12}	Th–9S = 3·00 A.
	Th–8S = 2·94 A.
ThS_2	Th–9S = 2·95 A.

A detailed discussion of the interatomic distances will be given in a subsequent article of this series.

Crystal Chemical Studies of the 5f-Series of Elements. X. Sulfides and Oxy-Sulfides

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A number of sulfides and oxy-sulfides of 5f-elements and of cerium have crystal structures of known types as follows:

NaCl-type:	CeS, ThS, US, PuS,
Sb_2S_3-type:	Th_2S_3, U_2S_3, Np_2S_3,
$PbCl_2$-type:	ThS_2,
PbFCl-type:	ThOS, UOS, NpOS.

The crystal structures of some sulfides and oxy-sulfides of 5f-elements and of lanthanum and cerium were described in earlier articles of this series (Zachariasen, 1948 a–e, 1949 a–d). Additional crystal-structure data for sulfides and oxy-sulfides of these elements are presented in this paper.

The results for thorium, uranium and cerium sulfides are the outcome of systematic studies of the systems Th–S, U–S and Ce–S. This work was carried out in cooperation with Prof. Leo Brewer of the University of California, who provided the writer with a large number of sulfide preparations of these elements. The results on the chemistry and thermodynamics of the sulfides will be published elsewhere by Prof. Brewer.

The sulfides of the transuranic elements were encountered in miscellaneous micro-preparations, which the writer was asked to investigate for the purpose of chemical identification.

1. Survey of the phases

Cerium sulfides

Prof. Brewer submitted a series of cerium sulfide preparations covering the range $S : Ce = 0.80-1.50$. The X-ray diffraction patterns showed the existence of two sulfide phases. One of these is the $Ce_2S_3-Ce_3S_4$ phase which has a homogeneity range extending from $S : Ce = 1.33$ to $S : Ce = 1.50$. The other phase is CeS with a sharply defined composition.

Prof. Brewer also furnished a number of cerium oxy-sulfide preparations with different oxygen contents. Ce_2O_2S is the only oxy-sulfide observed in these preparations.

Thorium sulfides

X-ray diffraction patterns were taken of numerous sulfide samples in the range $S : Th = 0.8-2.0$. Four thorium sulfide phases exist in this range. These are ThS, Th_2S_3, Th_7S_{12} and ThS_2. The homogeneity range of the phase Th_7S_{12} extends from $S : Th = 1.71$ to $S : Th = 1.76$. The phases ThS, Th_2S_3 and ThS_2 have sharply defined chemical compositions.

A single thorium oxy-sulfide preparation was examined. It was found to contain about 80 % ThOS, the second phase being ThS_2.

Uranium sulfides

Uranium sulfide samples in the range $S : U = 1.0-2.0$ were studied. Only the phases US, U_2S_3 and US_2, all with sharply defined chemical formulas, exist. In contrast to the Th–S system there is no intermediate phase between U_2S_3 and US_2.

Dr L. B. Arnold procured for the writer a sample of unknown origin and labelled 'US$_2$ 80 %'. The X-ray diffraction pattern showed the sample to contain a single phase which could be identified as UOS. The same phase was later observed in a sample of UOS obtained from Prof. Brewer. The composition of the latter preparation had been confirmed by direct chemical analysis.

Plutonium sulfides

The first micro-preparations of plutonium sulfides were made by Dr N. R. Davidson by reacting H_2S with PuO_2 at high temperatures. The X-ray examination showed that one of Dr Davidson's preparations contained a single phase which was isostructural with Ce_2S_3, and which hence was identified as Pu_2S_3. Another preparation was found to contain about 30 % PuO_2 and 70 % of a phase isostructural with Ce_2O_2S. The latter phase was thus identified as Pu_2O_2S.

Dr E. F. Westrum attempted a calcium reduction of PuF_3 in a barium sulfide crucible. On the basis of a microscopic examination Dr Westrum suspected that a plutonium sulfide might have been formed by reaction with the crucible and asked the writer to examine the reaction product. The X-ray diffraction pattern showed that 85 % of the sample consisted of a phase isostructural with NaCl. It could be concluded on the basis of unit-cell dimensions and diffraction intensities that the unknown phase had to be either BaO or PuS. In order to distinguish between the two possibilities Dr Westrum ignited the sample. Since the X-ray diffraction pattern showed the bulk of the ignited sample to be PuO_2, it proved that the initial phase was PuS and not BaO.

Neptunium sulfides

Drs Sherman Fried and N. R. Davidson were the first to try to make neptunium sulfide. Their preparations were made on the microgram scale. The X-ray diffraction pattern showed that the first attempt led to a single phase which was isostructural with ThOS and UOS, and which hence was identified as NpOS. Samples resulting from subsequent attempts were found to contain a phase which was identified as Np_2S_3 because it was isostructural with Th_2S_3 and U_2S_3.

Americium and actinium sulfides

An americium sulfide preparation by Dr Sherman Fried and an actinium sulfide preparation by Drs Fried and F. Hagemann proved on X-ray examination to be single-phase samples. Since the compounds were found to be isostructural with Ce_2S_3 they were identified as Am_2S_3 and Ac_2S_3.

Table 1 lists the sulfides and oxy-sulfides which so far have been observed for 5*f*-elements and for lanthanum and cerium. Compounds given in the same horizontal row are isostructural.

Table 1. *List of sulfides and oxy-sulfides*

	CeS		ThS	US		PuS	
La$_2$S$_3$	Ce$_2$S$_3$–Ce$_3$S$_4$	Ac$_2$S$_3$				Pu$_2$S$_3$	Am$_2$S$_3$
			Th$_2$S$_3$	U$_2$S$_3$	Np$_2$S$_3$		
			Th$_7$S$_{12}$				
				US$_2$			
			ThS$_2$				
La$_2$O$_2$S	Ce$_2$O$_2$S					Pu$_2$O$_2$S	
			ThOS	UOS	NpOS		

The crystal structures of La_2S_3, $Ce_2S_3-Ce_3S_4$, Ac_2S_3, Pu_2S_3, Am_2S_3, Th_7S_{12}, La_2O_2S, Ce_2O_2S and Pu_2O_2S have been discussed in earlier papers of this series. The crystal structure of US_2 is being investigated by Dr R. C. L.

Mooney. The results of the crystal-structure investigations for the remaining compounds listed in Table 1 are presented in the following sections.

All X-ray diffraction patterns were taken with Cu K radiation filtered through nickel foil. Single crystal splinters of Th_2S_3 and U_2S_3 were isolated so that Weissenberg data could be obtained. The other compounds were available only in microcrystalline form, and hence the structure investigations had to be based on powder diffraction data.

2. The crystal structure of CeS, ThS, US and PuS

The diffraction data for CeS and PuS are given in Table 2, while Table 3 lists the observed intensities for all four compounds.

Table 2. *Diffraction data for* CeS *and* PuS

	CeS		PuS	
ΣH_i^2	$\sin^2 \theta$	$I_{obs.}$	$\sin^2 \theta$	$I_{obs.}$
3	0·0543	$w+$	0·0603	$m+$
4	0·0725	$s+$	0·0797	$m+$
8	0·1436	s	0·1581	s
11	0·1976	m	0·2167	s
12	0·2148	$w+$	0·2361	w
16	0·2859	$w+$	0·3140	$w-$
19	0·3397	$w+$	0·3716	wm
20	0·3575	s	0·3909	$m+$
24	0·4292	$m+$	0·4676	m
27	0·4820	w	0·5262	$m-$
32	0·5701	$w-$	0·6216	w
35	0·6232	$w+$	0·6797	s
36	0·6413	m	0·6994	s
40	0·7124	$m-$	0·7760	s
43	0·7661	vw	0·8335	wm
44	0·7832	$m-$	0·8525	s
48	0·8537	vw	0·9291	w
51	0·9071	$m-$	0·9871	s
52	0·9249	m		

Table 3. *Observed and calculated intensities for monosulfides*

	CeS		PuS	US	ThS	
ΣH_i^2	$\lvert F \rvert^2 p$	$I_{obs.}$	$I_{obs.}$	$I_{obs.}$	$I_{obs.}$	$\lvert F \rvert^2 p$
3	11	$w+$	$m+$	m	$s-$	37
4	21	$s+$	$m+$	s	$s+$	46
8	34	s	s	s	s	77
11	23	m	s	s	$s-$	82
12	19	$w+$	w	$w+$	$w+$	45
16	12	$w+$	$w-$	w	$w+$	29
19	17	$w+$	wm	$w+$	$w+$	62
20	44	s	$m+$	s	$m+$	108
24	42	$m+$	m	m	m	98
27	20	w	$m-$	m	$m-$	76
32	16	$w-$	w	w	w	41
35	25	$w+$	s	m	$m-$	91
36	41	m	s	$s-$	m	102
40	30	$m-$	s	s	$m-$	72
43	12	vw	wm	$w+$	$w-$	43
44	28	$m-$	s	s	$w+$	70

It is readily seen that the observed intensities are compatible only with the sodium chloride type of structure. Calculated values of $\lvert F \rvert^2 p$ (p being the multiplicity factor) for CeS and ThS are given in Table 3.

Unit-cell dimensions and calculated densities are:

	a (kX.)	ρ (g.cm.$^{-3}$)
CeS	5·766 ± 0·002	5·93
ThS	5·671 ± 0·002	9·56
US	5·473 ± 0·002	10·87
PuS	5·525 ± 0·001	10·60

A phase having a composition varying between $ThS_{0.50}$ and $ThS_{0.75}$ has been reported in the literature (Strotzer & Zumbusch, 1941). The structure of the phase is given as deficit NaCl structure with $a = 5\cdot674$ A. Evidently this is the same phase as the thorium monosulfide of the present paper.

The conclusions of the earlier workers as to the chemical composition cannot be confirmed. According to the present investigation the phase is characterized by a ratio S : Th = 1·0. This is shown by the fact that thorium sulfide preparations with S : Th = 0·835 and 0·85 were found to contain 10–20 % of metallic thorium.

CeS, ThS and US form solid solutions. Some of the observed unit-cell constants for these mixtures are:

Composition	a (kX.)
67 % CeS, 33 % ThS	5·725 ± 0·003
50 % CeS, 50 % ThS	5·709 ± 0·003
33 % CeS, 67 % ThS	5·701 ± 0·003
50 % ThS, 50 % US	5·587 ± 0·003

3. The crystal structure of Th_2S_3, U_2S_3 and Np_2S_3

Needle-shaped single-crystal splinters of Th_2S_3 and U_2S_3 weighing 0·4 and 0·2 micrograms were used to make complete sets of Weissenberg patterns about the needle axis (the a_3 axis).

The powder diffraction pattern of Np_2S_3 was poor, and indexing was difficult because the pattern is so rich in diffraction lines. As a consequence the unit-cell dimensions of Np_2S_3 are only approximately known.

The three compounds are orthorhombic with unit-cell dimensions as follows:

	a_1 (kX.)	a_2 (kX.)	a_3 (kX.)
Th_2S_3	10·97 ± 0·05	10·83 ± 0·05	3·95 ± 0·03
U_2S_3	10·39 ± 0·02	10·63 ± 0·02	3·88 ± 0·01
Np_2S_3	10·3 ± 0·1	10·6 ± 0·1	3·85 ± 0·05

In the unit cell there is room for but four molecules. The calculated densities are thus $\rho = 7\cdot87$ for Th_2S_3, $\rho = 8\cdot78$ for U_2S_3 and $\rho \approx 8\cdot8$ g.cm.$^{-3}$ for Np_2S_3.

The translation lattice is primitive, but the Weissenberg data for Th_2S_3 and U_2S_3 show that reflections $H_1 0 H_3$ are absent if $H_1 + H_3$ is odd and that reflections $0 H_2 H_3$ are absent if H_2 is odd. Assuming holohedral symmetry the space group is $Pbnm$–D_{2h}^{16}. It is necessary to place all atoms in reflection planes, otherwise metal–metal and sulfur–sulfur distances would be impossibly small. Choosing the origin in an inversion center the atomic coordinates are: $\pm (x, y, \frac{1}{4})$; $(\frac{1}{2} - x, y + \frac{1}{2}, \frac{1}{4})$.

The four parameters for the metal atoms are readily determined from the intensity data for Th_2S_3 and U_2S_3. The observed intensities require slightly different metal parameters for the two compounds. The contribution of

the sulfur atoms to the structure factor is too small to permit a direct determination of the six sulfur parameters. Spatial considerations showed, however, that there is only one way of placing the sulfur atoms if unreasonably short metal–sulfur or sulfur–sulfur distances are to be avoided. The parameter values for Th_2S_3 and U_2S_3 deduced in this manner are tabulated in Table 4, while observed intensities and calculated structure factors (per stoichiometric molecule) for U_2S_3 are given in Table 5.

Table 4. Parameter values for Th_2S_3 and U_2S_3 compared with those for Sb_2S_3

	x	y		x	y
U_I	·0·311 ± 0·003	−0·014 ± 0·003	Sb_I	0·328	0·031
Th_I	0·314 ± 0·003	−0·022 ± 0·003			
U_{II}	0·508 ± 0·003	0·305 ± 0·003	Sb_{II}	0·539	0·351
Th_{II}	0·519 ± 0·003	0·300 ± 0·003			
S_I	0·878	0·053	S_I	0·883	0·047
S_{II}	0·561	0·871	S_{II}	0·561	0·875
S_{III}	0·206	0·230	S_{III}	0·194	0·208

The configuration of sulfur atoms about metal atoms is as follows:

$$U_2S_3$$

$$\begin{array}{ll} U_I\text{--}2\,S_I = 2\cdot79\,A. & U_{II}\text{--}2\,S_I = 2\cdot81\,A. \\ \quad\text{--}2\,S_{II} = 2\cdot80 & \quad\text{--}1\,S_I = 2\cdot90 \\ \quad\cdot1\,S_{II} = 2\cdot88 & \quad\text{--}2\,S_{II} = 2\cdot79 \\ \quad\text{--}1\,S_{III} = 2\cdot73 & \quad\text{--}2\,S_{III} = 2\cdot86 \\ \quad\text{--}1\,S_{III} = 2\cdot82 & (\text{--}1\,S_{III} = 3\cdot24) \end{array}$$

Mean value U–S = 2·82 A.

$$Th_2S_3$$

$$\begin{array}{ll} Th_I\text{--}2\,S_I = 2\cdot91\,A. & Th_{II}\text{--}1\,S_I = 2\cdot96\,A. \\ \quad\text{--}2\,S_{II} = 2\cdot91 & \quad\text{--}2\,S_I = 2\cdot97 \\ \quad\text{--}1\,S_{II} = 2\cdot94 & \quad\text{--}2\,S_{II} = 2\cdot84 \\ \quad\text{--}1\,S_{III} = 2\cdot83 & \quad\text{--}2\,S_{III} = 2\cdot86 \\ \quad\text{--}1\,S_{III} = 2\cdot86 & (\text{--}1S_{III} = 3\cdot56) \end{array}$$

Mean value Th–S = 2·90 A.

Table 5. Weissenberg intensities for U_2S_3

$H_1H_2H_3$	$I_{obs.}$	$\lvert F \rvert$	$H_1H_2H_3$	$I_{obs.}$	$\lvert F \rvert$
200	vw	26	061	w	71
400	w	82	081	Nil	20
600	w+	106	0.10.1	Nil	27
800	Nil	11	0.12.1	m−	95
10.0.0	w	87			
12.0.0	vw−	27	110	Nil	4
			220	m	110
020	vw	15	330	Nil	4
040	m	88	440	Nil	1
060	w	87	550	Nil	8
080	Nil	15	660	w	65
0.10.0	w	99	770	Nil	11
0.12.0	Nil	10	880	w+	96
101	s	72	111	m	60
301	m	67	221	wm	51
501	w	46	331	vw−	24
701	w−	37	441	wm	56
901	w	86	551	vw+	35
11.0.1	Nil	2	661	w+	73
			771	vw+	37
021	m	68	881	w	51
041	w+	55			

The shortest S–S distances in U_2S_3 are:

$$S_{II}\text{--}S_{III} = 3\cdot16 \text{ and } 3\cdot28, \quad S_I\text{--}S_{III} = 3\cdot51,$$
$$S_{II}\text{--}S_{II} = 3\cdot59 \text{ and } S_I\text{--}S_{II} = 3\cdot44\,A.$$

Th_2S_3, U_2S_3 and Np_2S_3 may be said to have the Sb_2S_3 type of structure. The sulfur parameters given by Hoffman (1933) for Sb_2S_3 are nearly the same as those found in this paper for Th_2S_3 and U_2S_3. However, the parameter values for antimony are considerably different from the ones found for thorium and uranium as Table 4 shows.

4. The crystal structure of ThS_2

Table 6 gives the results of the measurements of the diffraction lines in the first part of the powder pattern of ThS_2. The observed sine squares fit an orthorhombic quadratic form. The unit-cell dimensions as determined from the back-reflection region are:

$$a_1 = 4\cdot259 \pm 0\cdot002, \quad a_2 = 7\cdot249 \pm 0\cdot003,$$
$$a_3 = 8\cdot600 \pm 0\cdot003 \text{ kX}.$$

There are four molecules in the unit cell giving a calculated density of $\rho = 7\cdot36$ g.cm.$^{-3}$.

Table 6. Powder diffraction data for ThS_2

$\sin^2\theta$	$I_{obs.}$	$H_1H_2H_3$	$\sin^2\theta$	$I_{obs.}$	$H_1H_2H_3$
0·0414	w+	101	0·1516	m	123
0·0441	s	012	0·1755	s	220, 024, 212
0·0460	w	020	0·1825	vw	040
0·0532	m	111	0·2082	w−	133
0·0776	vw	112, 120	0·2227	w−	141
0·0870	s−	121	0·2464	w+	115
0·1062	w+	103	0·2613	w−	204
0·1121	vvw	031, 122	0·2665	m	232
0·1177	m−	113	0·2797	w	125
0·1298	w−	004	0·2880	w	143
0·1324	w−	200	0·3021	w	301, 016
0·1358	m	032	0·3060	w+	224
0·1439	m	131			

The space group is $Pmnb$–D_{2h}^{16}, and the structure is of the $PbCl_2$ type. One set of four thorium atoms and two sets of four sulfur atoms are in reflection planes at positions:

$$\pm(\tfrac{1}{4}, y, z); (\tfrac{1}{4}, \tfrac{1}{2}+y, \tfrac{1}{2}-z).$$

The six parameter values were determined. The two thorium parameters were readily fixed from intensity considerations, while the sulfur parameters were adjusted so as to give reasonable interatomic distances. The parameter values so obtained are as follows:

	y	z
Th	0·250 ± 0·010	−0·125 ± 0·010
S_I	−0·150	−0·068
S_{II}	−0·035	0·320

Observed intensities and calculated values $\lvert F \rvert^2 p$ are compared in Table 7.

Each thorium atom is bonded to nine sulfur atoms with an average distance of Th–S = 2·95 A., the individual values being

$$Th\text{--}1\,S_I = 2\cdot74, \quad Th\text{--}1\,S_I = 2\cdot94, \quad Th\text{--}2\,S_I = 2\cdot80,$$
$$Th\text{--}2\,S_{II} = 3\cdot00, \quad Th\text{--}1\,S_{II} = 3\cdot05 \text{ and } Th\text{--}2\,S_{II} = 3\cdot13\,A.$$

The smallest S–S separations are

$$S_I\text{--}S_I = 3\cdot26, \quad S_I\text{--}S_{II} = 3\cdot27 \text{ and } 3\cdot32\,A.$$

Table 7. *Intensities for* ThS_2

$H_1H_2H_3$	$\lvert F\rvert^2 p$	$I_{obs.}$	$H_1H_2H_3$	$\lvert F\rvert^2 p$	$I_{obs.}$
011	0	Nil	031	0·4	
002	0	Nil	122	1·0	*vvw*
101	10·0	*w+*	113	24·8	*m−*
012	20·8	*s*	023	0·5	Nil
020	9·8	*w*	004	11·2	*w−*
111	20·0	*m*	200	17·0	*w−*
021	0	Nil	032	26·8	*m*
022	0·2	Nil	014	0·1	Nil
112	1·4		131	23·2	*m*
120	1·1	*vw*	123	18·4	*m*
013	0·6	Nil	211	0·1	Nil
121	32·0	*s−*	132	0	Nil
103	16·8	*w+*			

5. The crystal structure of ThOS, UOS and NpOS

Powder diffraction data for UOS and NpOS are given in Tables 8 and 9. The observations correspond to tetragonal symmetry and primitive translation group. Measurements in the back-reflection region gave the following unit-cell dimensions:

	a_1 (kX.)	a_3 (kX.)	ρ (g.cm.$^{-3}$)
ThOS	3·955 ± 0·002	6·733 ± 0·004	8·78
UOS	3·835 ± 0·001	6·681 ± 0·001	9·60
NpOS	3·817 ± 0·002	6·641 ± 0·010	9·71

The densities, ρ, given above are calculated for two stoichiometric molecules.

The structure type is evidently that of PbFCl with space group $P4/nmm–D_{4h}^7$ and atomic positions as follows:

$$2\,\text{Th}, 2\,\text{U or } 2\,\text{Np in } (\tfrac{1}{2}, 0, u_1); \ (0, \tfrac{1}{2}, \bar{u}_1).$$
$$2\,\text{O} \quad \text{in } (0, 0, 0); \ (\tfrac{1}{2}, \tfrac{1}{2}, 0).$$
$$2\,\text{S} \quad \text{in } (\tfrac{1}{2}, 0, u_2); \ (0, \tfrac{1}{2}, \bar{u}_2).$$

The intensities of reflections with high values of H_3 require $u_1 = 0\cdot200 \pm 0\cdot006$ for all three compounds. The sulfur parameter cannot be accurately determined from the observed intensities. The values $u_2 = 0\cdot647$ for ThOS and $u_2 = 0\cdot638$ for UOS and NpOS were adopted. With these values each metal atom is placed equidistant from the five nearest sulfur atoms.

Table 8. *Powder diffraction data for* UOS *and* NpOS

UOS		NpOS		
$\sin^2\theta$	$I_{obs.}$	$\sin^2\theta$	$I_{obs.}$	$H_1H_2H_3$
0·0550	*s*	0·0543	*s*	101, 002
0·0822	*m*	0·0818	*m−*	110
0·0956	*m*	0·0951	*m−*	102
0·1217	*vw−*	—	—	003
0·1358	*m*	0·1360	*m−*	112
0·1632	*m*	0·1630	*m−*	200, 103
0·1766	*vw−*	—	—	201
0·2029	*w*	0·2037	*w−*	113
0·2174	*s*	0·2177	*m+*	211, 202
0·2567	*m+*	0·2573	*m−*	212, 104
0·2827	*w−*	0·2835	*vw*	203
0·3242	*m*	0·3254	*w+*	220, 213
0·3346	*vw+*	—	—	005
0·3779	*m*	0·3804	*w*	301, 222
0·4048	*m*	0·4070	*w*	310
0·4163	*s*	0·4190	*m*	302, 214, 115
0·4441	*w−*	—	—	223
0·4583	*m*	0·4615	*w−*	312
0·4838	*w−*	0·4874	*vw−*	303
0·4958	*m−*	0·4991	*vw+*	205

Table 9. *Spectrometer data for* UOS

		Intensity	
$H_1H_2H_3$	$\sin^2\theta$	Obs.	Calc.
002, 101	0·0537	99	26+119
110	0·0807	49	62
102, 111	0·0935	44	45+2
003	0·1198	5	6
112	0·1340	41	43
103, 200	0·1606	39	16+28
201	0·1740	5	3
113	0·1998	18	15
004, 202, 211	0·2139	49	0+15+34
104, 212	0·2530	29	19+20
203	0·2804	7	6
114	—	0	0
213, 220	0·3208	21	10+9
005	0·3310	6	3
221	—	0	1
105, 204	—	0	0+1
222, 301	0·3740	15	7+7
310	0·4012	11	11

The intensities calculated for UOS on the basis of this structure are given in the last column of Table 9. The following intensity formula was used:

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

The interatomic distances are:

Th–4 O = 2·40 A., U–4 O = 2·34 A., Np–4 O = 2·32 A.,
Th–5 S = 3·00 A., U–5 S = 2·93 A., Np–5 S = 2·91 A.

6. Concluding remarks

Many of the crystal-structure results obtained for the sulfides of the 5*f*-elements are at first sight difficult to understand.

It is observed for instance that the metal–sulfur distance does not increase from ThS_2 to Th_2S_3 to ThS as one would expect with the decreasing formal valence of thorium.

It may also seem puzzling that the sesqui-sulfides of americium and plutonium are isostructural with actinium sesqui-sulfide while the sesqui-sulfides thorium, uranium and neptunium have a different structure.

These and other observations of rather unexpected nature can be satisfactorily interpreted with the aid of the metallic-covalent radii for the 5*f*-elements. The conclusion is briefly that the monosulfides, the sesquisulfides of thorium, uranium, neptunium, and the compound Th_7S_{12} must be regarded as subsulfides in which the metal atoms are essentially tetravalent. The oxysulfides, the sesqui-sulfides of actinium, plutonium, americium, and thorium disulfide are on the other hand normal valence compounds.

A detailed discussion of the interatomic distances observed in the sulfides will be given in a later article of this series dealing with the crystal radii of the 4*f*- and 5*f*-elements.

The writer is greatly indebted to Prof. Leo Brewer for the numerous sulfide samples. Drs N. R. Davidson, Sherman Fried, F. Hagemann and E. F. Westrum kindly

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

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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-UF₅ is tetragonal body-centered with $a_1 = 6.512 \pm 0.001$, $a_3 = 4.463 \pm 0.001$ kX. and two stoichiometric molecules per unit cell. In the proposed structure each uranium atom is bonded to six fluorine atoms. The UF₆ octahedra are linked by shared corners into endless strings along the a_3 axis.

β-UF₅ is also tetragonal body-centered. The unit cell containing eight stoichiometric molecules has dimensions $a_1 = 11.450 \pm 0.002$, $a_3 = 5.198 \pm 0.001$ kX. A structure is proposed in which each uranium atom is bonded to seven fluorine atoms.

The interatomic distances are:

$$\alpha\text{-UF}_5, \quad \text{U–6 F} = 2.20 \text{ A.}$$
$$\beta\text{-UF}_5, \quad \text{U–7 F} = 2.23 \text{ A.}$$
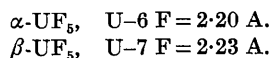
Uranium pentafluoride was first described in 1911 (Ruff & Heinzelmann, 1911). The compound was prepared in the course of war work within the Manhattan Project. P. Agron, A. Grenall, R. Kunin & S. Weller (*Manhattan Project Reports*) showed by means of X-ray diffraction patterns that uranium pentafluoride 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-UF₅ up to $\sin^2\theta = 0.400$. The observations correspond to a tetragonal body-centered translation group. The unit-cell dimensions as deduced from measurements in the back-reflection region are:

$$a_1 = 6.512 \pm 0.001, \quad a_3 = 4.463 \pm 0.001 \text{ kX.}$$

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

Observed intensity	$\sin^2\theta$	$H_1H_2H_3$	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