8. Compound isostructural with K_3ZrF_7

The alpha form of K_3UF_7 is cubic with $a = 9.21 \pm 0.01$ kX. and four molecules per unit cube. The structure type is that of K_3ZrF_7.

9. Compound isostructural with Cu_2Mg

$CePt_2$ is cubic with $a = 7.714 \pm 0.001$ kX. and eight molecules per unit cube. The structure type is that of Cu_2Mg. The atomic configuration and the interatomic distances are:

$$Ce-12\,Pt = 3.198\,kX., \quad Ce-4\,Ce = 3.340\,kX.,$$
$$Pt-6\,Pt = 2.727\,kX. \quad and \quad Pt-6\,Ce = 3.198\,kX.$$

10. Compound isostructural with $CaTiO_3$

$CeAlO_3$ has the perowskite type of structure. The compound is tetragonal pseudo-cubic with

$$a_1 = 3.760 \pm 0.004\,kX., \quad a_3 = 3.787 \pm 0.004\,kX.$$

11. Compound isostructural with UO_2F_2

Neptunyl fluoride, NpO_2F_2, has the uranyl fluoride type of structure (Zachariasen, 1948).

The rhombohedral unit cell containing one molecule has dimensions $a = 5.784 \pm 0.005$ kX., $\alpha = 42° 16' \pm 10'$.

Referred to hexagonal axes the cell dimensions of UO_2F_2 and NpO_2F_2 are:

	a_1 (kX.)	a_3 (kX.)
UO_2F_2	4.198 ± 0.001	15.661 ± 0.010
NpO_2F_2	4.170 ± 0.005	15.77 ± 0.03

It is seen that the interatomic distances within the layers are smallest for NpO_2F_2. However, the binding between the layers is stronger for UO_2F_2 than it is for NpO_2F_2.

12. Compound isostructural with hexagonal $LaPO_4$

$AcPO_4 . 0.5H_2O$ is hexagonal and is isostructural with the analogous lanthanum compound (Mooney, 1948). The unit-cell dimensions are

$$a_1 = 7.21 \pm 0.02\,kX., \quad a_3 = 6.64 \pm 0.03\,kX.$$

13. Compound isostructural with UCl_4

$NpCl_4$ is tetragonal and isostructural with UCl_4 (Mooney, 1949). The unit-cell dimensions are

$$a_1 = 8.25 \pm 0.01\,kX., \quad a_3 = 7.46 \pm 0.01\,kX.$$

With chlorine parameter values $x = 0.310$ and $z = 0.430$ the interatomic distances become

$$Np-4\,Cl = 2.61\,A. \quad and \quad Np-4\,Cl = 2.86\,A.$$

Other examples of known structure types have been reported in earlier papers of the present series as follows:

Type	Compounds	Article no.
NaCl	ThS, US, PuS, CeS	X
PbFCl	ThOS, UOS, NpOS	X
Sb_2S_3	Th_3S_3, U_2S_3, Np_2S_3	X
$PbCl_2$	ThS_2	X
$ThSi_2$	α-USi_2, $NpSi_2$, $PuSi_2$, $CeSi_2$	VIII
AlB_2	β-USi_2	VIII
FeB	USi	VIII
Th_3P_4	Ac_2S_3, Pu_2S_3, Am_2S_3	
	La_2S_3, Ce_2S_3–Ce_3S_4	VI
K_2GeF_6	Cs_2PuCl_6	II

References

FANKUCHEN, I. (1935). *Z. Krystallogr.* **91**, 473.
MOONEY, R. C. L. (1948). *J. Chem. Phys.* **16**, 1003.
MOONEY, R. C. L. (1949). *Acta Cryst.* **2**, 189.
OFTEDAL, I. (1931). *Z. phys. Chem.* B, **13**, 190.
PAULING, L. (1928). *Z. Krystallogr.* **69**, 415.
SCHULZE, G. E. R. (1934). *Z. Krystallogr.* **89**, 477.
ZACHARIASEN, W. H. (1948). *Acta Cryst.* **1**, 277.

Crystal Chemical Studies of the 5f-Series of Elements.
XIII. The Crystal Structure of U_2F_9 and $NaTh_2F_9$

By W. H. ZACHARIASEN

Argonne National Laboratory and the Department of Physics, University of Chicago, Chicago, Illinois, U.S.A.

The compound U_2F_9 is cubic body-centered with $a = 8.4545 \pm 0.0005$ kX. and four stoichiometric molecules per unit cube. The positions of the uranium atoms have been determined from the observed intensities and the positions of the fluorine atoms from spatial considerations. Each uranium atom is bonded to nine fluorine atoms with U–9 F = 2.31 A. The uranium atoms are structurally equivalent.

The double fluoride, $NaTh_2F_9$, is cubic body-centered with $a = 8.705 \pm 0.005$ kX. The positions of the thorium and fluorine atoms are practically the same as for the uranium and fluorine atoms in the U_2F_9 structure. Suitable positions for the sodium atoms have been found. The interatomic distances are Na–6 F = 2.34 A. and Th–9 F = 2.40 A.

Dr Ralph Livingston (1943) is the first to have prepared the compound now known to be U_2F_9. The black substance, which on exposure to air turns into green UF_4, was obtained in the course of an attempt to make UF_5. Dr Livingston asked me to examine his product.

The interpretation of the X-ray diffraction patterns

showed the sample to consist of a single phase with a cubic body-centered translation lattice and a cube edge of $8\cdot455 \pm 0\cdot002\,\mathrm{kX}$. It was further shown that the unit cube contained eight uranium atoms in positions:

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

$$(u,u,u),\ (u,\bar{u},\bar{u})\diagdown$$

with $u = 0\cdot187 \pm 0\cdot004$ (Zachariasen, 1943).

I had shown that the volume requirement of a fluorine (or oxygen atom) in uranium or thorium compounds was 18–$19\,\mathrm{A.^3}$ Accordingly, the unit cell of the black fluoride could accommodate about 33 fluorine atoms. The value of 18–$19\,\mathrm{A.^3}$ for the volume requirement of a fluorine atom being accurate to about 10 % the formula $\mathrm{UF_5}$ could be ruled out, and I concluded that the black fluoride was a new form of $\mathrm{UF_4}$. Chemical analyses which were carried out at the time gave F : U ratios in the range $4\cdot0$–$4\cdot2$, in apparent confirmation of the chemical formula proposed by me.

The 'black fluoride' was later encountered in several of the other laboratories associated with the Manhattan Project. Improved methods of fluorine analysis made possible more accurate determination of the F : U ratio, and Weller, Grenall & Kunin (1945) were thus able to show that the chemical formula of the 'black fluoride' was $\mathrm{U_2F_9}$ and not $\mathrm{UF_4}$ as I had suggested.

The crystal structure of $\mathrm{U_2F_9}$*

Table 1 shows the observed sine squares up to $\sin^2\theta = 0\cdot500$ as obtained from powder-diffraction patterns of $\mathrm{U_2F_9}$ using Cu K radiation filtered through nickel foil. Measurements in the back-reflection region gave for the edge of the unit cube

$$a = 8\cdot4545 \pm 0\cdot0005\,\mathrm{kX}.$$

With four stoichiometric molecules $\mathrm{U_2F_9}$ per unit cube the calculated density is $\rho = 7\cdot06\,\mathrm{g.cm.^{-3}}$

The observed intensities require eight uranium atoms per cube in the positions:

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

$$8\,\mathrm{U\ in}\ (u,u,u),\ (u,\bar{u},\bar{u})\diagdown$$

with $u = 0\cdot187 \pm 0\cdot004$. It was readily shown that this is a unique solution. The last column of Table 1 gives the intensities as calculated on the basis of the uranium positions. The following intensity formula was used:

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

where p is the permutation factor.

The eightfold positions found for uranium correspond to space groups $I23\text{–}T^3$, $P\bar{4}3n\text{–}T_d^4$ and $I\bar{4}3m\text{–}T_d^3$, the first being a subgroup of the last.

Because of the small scattering power of fluorine

---

* The principal results have already been published (Zachariasen, 1948c).

relative to uranium it did not prove feasible to determine the fluorine positions from the powder diffraction data. It was therefore attempted to locate the fluorine atoms by means of spatial considerations. This attempt was successful. The fluorine positions, which correspond to the space group $I\bar{4}3m$, are (Zachariasen, 1945)

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

$$12\,\mathrm{F_I\ in} \pm (x,0,0)\diagdown$$

with $x = 0\cdot225$,

$$24\,\mathrm{F_{II}\ in}\ (x,x,z)\diagdown;\ (x,\bar{x},\bar{z})\diagdown;\ (\bar{x},x,z)\diagdown;\ (\bar{x},\bar{x},z)\diagdown$$

with $x = 0\cdot20$ and $z = 0\cdot46$.

Table 1. *X-ray diffraction data for* $\mathrm{U_2F_9}$

		Intensity	
ΣH_i^2	$\sin^2\theta$	Obs.*	Calc.
4	0·0342	m	76
6	0·0507	ms	140
8	0·0676	$w-$	32
10	0·0847	$w-$	24
12	0·1011	$vw+$	13
14	0·1181	$w-$	32
16	—	Nil	0
18	0·1513	vs	87
20	—	Nil	0
22	0·1849	$m-$	23
24	0·2015	w	14
26	0·2178	$m-$	18
30	0·2511	$w-$	10
32	—	Nil	0
34	0·2840	m	24
36	0·3006	$m-$	18
38	0·3176	$m+$	30
40	0·3336	$w-$	6·0
42	0·3505	$w-$	5·4
44	0·3671	vw	5·1
46	0·3841	$w-$	4·8
48	0·4005	w	6·0
50	0·4168	$w+$	7·1
52	—	Nil	0
54	0·4498	$m+$	22
56	0·4658	$w+$	7·0
58	0·4834	vvw	1·7

* s = strong, m = medium, w = weak, vw = very weak.

It should be emphasized that the proposed arrangement of the fluorine atoms has not been directly deduced from intensity observations. However, I have not been able to find any other reasonable arrangement, and the proposed structure is probably correct.

Each uranium atom is bonded to nine fluorine atoms. The distances are:

$$\mathrm{U\text{-}3\,F_I} = 2\cdot26\,\mathrm{A.,\quad U\text{-}3\,F_{II}} = 2\cdot31\,\mathrm{A.}$$

and

$$\mathrm{U\text{-}3\,F_{II}} = 2\cdot34\,\mathrm{A.}$$

The mean value is thus

$$\mathrm{U\text{-}9\,F} = 2\cdot31\,\mathrm{A.}$$

The closest distances of approach between two fluorine atoms are:

$$\mathrm{F_I\text{-}F_I} = 2\cdot69\,\mathrm{A.,\quad F_I\text{-}F_{II}} = 2\cdot57\,\mathrm{A.}$$

and

$$\mathrm{F_{II}\text{-}F_{II}} = 2\cdot58\,\mathrm{A.}$$

U–F distances in the uranium pentafluoride structure

25-2

(Zachariasen, 1949) and in some compounds of tetravalent uranium (Zachariasen, 1948 a) are

$$\alpha\text{-UF}_5 \qquad U\text{-}6\,F = 2 \cdot 20\,\text{A.}$$
$$\beta\text{-UF}_5 \qquad U\text{-}7\,F = 2 \cdot 23\,\text{A.}$$
$$\beta_1\text{-K}_2\text{UF}_6 \qquad U\text{-}9\,F = 2 \cdot 36\,\text{A.}$$
$$\beta_2\text{-Na}_2\text{UF}_6 \qquad U\text{-}9\,F = 2 \cdot 38\,\text{A.}$$
$$\gamma\text{-Na}_2\text{UF}_6 \qquad U\text{-}8\,F = 2 \cdot 36\,\text{A.}$$
$$\text{Na}_3\text{UF}_7 \qquad U\text{-}8\,F = 2 \cdot 36\,\text{A.}$$

The deduced distance of $\ddot{U}\text{-}9\,F = 2 \cdot 31\,\text{A.}$ in U_2F_9 is thus entirely reasonable.

In spite of the fact that uranium has the fractional valence $4\frac{1}{2}$ in U_2F_9, the uranium atoms are structurally equivalent. It is hence improper to write the formula as $UF_4 . UF_5$ or $UF_6 . 3UF_4$. It must be concluded that the uranium atoms resonate between the valence states four and five. The fact that the color of U_2F_9 is black is no doubt a consequence of this resonance.

The crystal structure of NaTh₂F₉

In the system NaF–ThF₄ many phases exist (Zachariasen, 1948 b), and NaTh₂F₉ is one of them. I have prepared this phase by melting together NaF and ThF₄ in the mole ratio $1:2$. The ThF₄ material which was used in the preparation had been made by Dr Ralph Livingston. It was of high purity. Owing to sublimation of the sodium fluoride the composition of the melt is slightly shifted in the course of the preparation; and the excess thorium fluoride hydrolyses first to ThOF₂ and then to ThO₂ if the melting is carried out in air.

Table 2 shows the X-ray diffraction data of a typical melt for which the initial composition was $1\text{NaF} . 2\text{ThF}_4$. The measurements were made with the Norelco Spectrometer using Cu K radiation filtered through nickel foil. As indicated in the table, the sample was a mixture of NaTh₂F₉ and ThOF₂.

The diffraction pattern of NaTh₂F₉ is, except for a somewhat larger unit-cell constant, very similar to that of U_2F_9. Even in the back-reflection region there are only minor intensity differences between corresponding diffraction lines of U_2F_9 and NaTh₂F₉.

Back-reflection measurements give a value

$$a = 8 \cdot 705 \pm 0 \cdot 001\,\text{kX.}$$

for the edge of the unit cube of NaTh₂F₉. With four stoichiometric molecules per unit cube the calculated density is $\rho = 6 \cdot 58\,\text{g.cm.}^{-3}$

The observed intensities lead to exactly the same positions for the thorium atoms as were found for the uranium atoms in U_2F_9. A reasonable arrangement of the fluorine atoms in NaTh₂F₉ is obtained by the use of the fluorine positions of the U_2F_9 structure with but minor adjustments of the parameters. But it is not possible to place four sodium atoms per unit cell in accordance with the space-group symmetry observed for the thorium arrangement. An inspection of the U_2F_9 structure shows, however, that the sixfold positions of the space group $I\bar{4}3m$ are excellently suited for small cations. Indeed, these positions seem to be the only possible sites for the sodium atoms.

The structure for NaTh₂F₉ arrived at by these considerations is as follows (Zachariasen, 1945):

Space group $I\bar{4}3m\text{-}T_d^3$.

Atomic positions:

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

4 Na in $(\tfrac{1}{2},0,0)$,

8 Th in $(u,u,u); (u,\bar{u},\bar{u})$, with $u = 0 \cdot 187 \pm 0 \cdot 004$,

12 F_I in $\pm (x,0,0)$, with $x = 0 \cdot 235$,

24 F_{II} in (x,x,z) , $(x,\bar{x},\bar{z})$, $(\bar{x},x,\bar{z})$, $(\bar{x},\bar{x},z)$,

with $x = 0 \cdot 19$ and $z = 0 \cdot 465$.

Table 2. *Spectrometer data for* NaTh₂F₉

		NaTh₂F₉			ThOF₂	
Intensity (obs.)	$\sin^2\theta$ (obs.)	ΣH_i^2	$\sin^2\theta$ (calc.)	Intensity* (calc.)	$H_1 H_2 H_3$	$\sin_2\theta$ (calc.)
9	0·0155	2	0·0155	14	—	—
47	0·0310	4	0·0310	76	—	—
27	0·0447	—	—	—	002	0·0444
100	0·0469	6	0·0465	140	100	0·0480
36	0·0594	—	—	—	101	0·0591
25	0·0627	8	0·0620	32	—	—
13	0·0774	10	0·0775	24	—	—
11	0·0929	12	0·0930	13	102	0·0924
9	0·1087	14	0·1085	31	—	—
0	—	16	0·1240	0	—	—
78	0·1391	18	0·1395	87	—	—
28	0·1452	—	—	—	110	0·1440
17	0·1483	—	—	—	103	0·1479
0	—	20	0·1550	0	—	—
28	0·1713	22	0·1705	23	—	—
9	0·1860	24	0·1860	14	—	—
14	0·1887	—	—	—	112	0·1884
13	0·2026	26	0·2015	18	201	0·2031
3	0·2321	30	0·2325	10	—	—
0	—	32	0·2480	0	—	—
12	0·2630	34	0·2635	24	—	—
11	0·2793	36	0·2790	18	—	—
12	0·2942	38	0·2945	30	203	0·2919

* Intensity as calculated for U_2F_9. See Table 1.

About each sodium atom are six fluorine atoms with distances Na–2 $F_I = 2.31$ A. and Na–4 $F_{II} = 2.36$ A. Each thorium atom is bonded to nine fluorine atoms, the interatomic distances being

$$Th–3 F_I = 2.34 A., \quad Th–3 F_{II} = 2.42 A.$$
and $\quad\quad\quad\quad Th–3 F_{II} = 2.35 A.$

The mean distances are

$$Na–6 F = 2.34 A. \quad and \quad Th–9 F = 2.40 A.$$

The distances observed in other compounds are (Zachariasen, 1948 a):

β_1-K_2ThF_6 Th–9 F = 2.38 A.

β_2-Na_2ThF_6 Th–9 F = 2.42 A. and Na–6 F = 2.33 A.

NaF   Na–6 F = 2.31 A.

Clearly the $NaTh_2F_9$ structure is obtained from that of U_2F_9 by replacing uranium with thorium and by inserting the sodium atoms into octahedral 'holes'.

Attempts to prepare the analogous compound NaU_2F_9 have been unsuccessful. In the system NaF–UF_4 there is no phase between UF_4 and $NaUF_5$.

I am grateful to Dr Ralph Livingston for the samples of U_2F_9 and of ThF_4, and to Miss Anne Plettinger for having taken the diffraction patterns.

References

LIVINGSTON, R. (1943). *Manhattan Project Report*, CN-982.
WELLER, S., GRENALL, A. & KUNIN, R. (1945). *Manhattan Project Report*, A-3326.
ZACHARIASEN, W. H. (1943). *Manhattan Project Report*, CP-961.
ZACHARIASEN, W. H. (1945). *Manhattan Project Report*, CC-2753.
ZACHARIASEN, W. H. (1948a). *Acta Cryst.* 1, 265.
ZACHARIASEN, W. H. (1948b). *J. Amer. Chem. Soc.* 70, 2147.
ZACHARIASEN, W. H. (1948c). *J. Chem. Phys.* 16, 425.
ZACHARIASEN, W. H. (1949). *Acta Cryst.* 2, 296.

Structure of Thin Films of Silver and Silver Iodide on Silver Bromide Substrates*

BY CHESTER R. BERRY

Research Laboratories, Eastman Kodak Company, Rochester 4, N.Y., U.S.A.

The electron-diffraction reflection method has been used to examine thin deposits formed on large single crystals of silver bromide. Silver films were prepared by evaporation and silver iodide was formed by reaction of the silver bromide with dilute solutions of potassium iodide and of a cyanine iodide sensitizing dye. The various orientations and structures of these deposits can be accounted for by assuming that the coating layers are built up by a disordered stacking of close-packed layers on minute octahedral faces of the substrate. Comparison is made with related observations previously reported by others.

Thin films of silver and silver iodide on the surfaces of single crystals of silver bromide have been examined by the reflection technique of electron diffraction. These deposits are of particular interest because of the possibility of their occurrence in photographic processes.

Experimental

Crystals of silver bromide, in the shape of hemispheres 1 cm. or larger in diameter, were grown on an air-cooled platinum finger placed in contact with the surface of the melt. The melt was at roughly 15° C. above the melting-point, and the air velocity was crudely adjusted so that the grown crystal was ready to be raised from the melt in about 2 hr. Usually, more than one individual crystal was formed, but only single-crystal regions were used in the diffraction experiments. Since

cleavage faces cannot be made on silver bromide, flat faces were ground against sandpaper and then polished against filter paper moistened with ordinary photographic fixing solution. The existence of more than one crystal domain could be readily detected at this stage by the appearance of demarcation lines caused by different rates of etching in the various domains. From the electron-diffraction pattern Miller indices were assigned to the face, and, by further grinding and polishing at the appropriate angle to this face, a face having small indices could be formed. Since the (111) face is predominant in the usual precipitates of silver bromide, it is of special interest and was studied more than any others.

Deposits of silver were formed on these substrates by evaporation in the specimen chamber of the electron-diffraction instrument. The silver in the form of a fine wire was weighed and placed on a tantalum strip at