

(4) Evidence on the cleavage patterns seems to prove that this optical effect is directly related to a physically lamellar structure.

(5) Since lamellar structure is also observed in the other crystals, the postulate is submitted: (a) that these crystals grow by accretion of micelles, in keeping with the micellar theory for the solid state recently announced from this laboratory, (b) that the arsenate distributes itself unevenly between surface and interior of the micelle, in a sense segregating, (c) that the conventional layer-like accretion of these micelles therefore provides a lamellar structure in the present case whose inhomogeneity is intensified in a manner giving rise to the observed optical effects.

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Crystal Chemical Studies of the 5*f*-Series of Elements. XII. New Compounds Representing known Structure Types

BY W. H. ZACHARIASEN

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

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The paper summarizes crystal-structure information for fifty-five new compounds of 4*f*- and 5*f*-elements representing thirteen known structure types.

This paper summarizes crystal-structure results for a number of new compounds (of 4*f*- and 5*f*-elements) with structures corresponding to well-known types. The information is given without the supporting experimental evidence. Detailed accounts of the various investigations including experimental data will be published in future articles of the present series. The summary of the following pages is submitted for publication because the preparation of the complete papers has been delayed by unforeseen circumstances.

1. Compounds isostructural with NaCl

The unit-cell constants for compounds with the NaCl type of structure are listed in Table 1. These compounds have predominantly metallic character.

Table 1. NaCl type

Compound	<i>a</i> (kX.)	Compound	<i>a</i> (kX.)
NpO	5.00 ± 0.01	NpN	4.887 ± 0.002
PuO*	4.948 ± 0.002	PuN	4.895 ± 0.001
AmO†	4.95 ± 0.01	PuC	4.910 ± 0.005

* Result due to R. C. L. Mooney and W. H. Zachariasen.

† Degree of purity unknown.

2. Compounds isostructural with CaF₂

Table 2 contains the unit-cell constants for substances with the fluorite type of structure.

For PaO₂ one should expect *a* = 5.51 kX. by interpolation between ThO₂ and UO₂. The largest observed value for protactinium oxide preparations is

$$a = 5.45 \pm 0.01 \text{ kX.}$$

It is therefore suggested either that the preparations were impure, or that the composition of the investigated oxide is PaO_{2.2}, i.e. that the reduction of the tetravalent state is incomplete, and that there is a deficit of metal atoms or an excess of oxygen atoms in the structure.

Table 2. CaF₂ type

Compound	<i>a</i> (kX.)	Compound	<i>a</i> (kX.)
PaO _{2.2} ?	5.45 ± 0.01	α-K ₂ ThF ₆	5.994 ± 0.004
NpO ₂	5.425 ± 0.001	α-K ₂ UF ₆	5.934 ± 0.001
PuO ₂ *	5.386 ± 0.001	α-Na ₂ ThF ₆	5.676 ± 0.005
AmO ₂ †	5.377 ± 0.003	α-Na ₂ UF ₆	5.565 ± 0.004
AcOF	5.931 ± 0.002	α-KLaF ₄	5.932 ± 0.001
PuOF	5.70 ± 0.01	α-KCeF ₄	5.894 ± 0.001

* Result due to R. C. L. Mooney and W. H. Zachariasen.

† Degree of purity unknown.

The alpha phase of the compounds A₂XF₆ and AXF₄ is formed by quenching from the melt (Na₂ThF₆, Na₂UF₆, KLaF₄, KCeF₄) or by rapid precipitation from solution (K₂ThF₆, K₂UF₆). The A atoms and the X atoms are randomly distributed over the metal sites of the fluorite structure. Thus the unit cell contains $\frac{4}{3}$ molecules A₂XF₆ and two molecules AXF₄.

The compounds A₂XF₆ as well as the compounds AXF₄ have a wide homogeneity range corresponding to unit cell contents of

$$A_{4-k}X_kF_{4+3k}, \quad 1.33 \leq k \leq 1.60 \quad \text{for } A_2XF_6,$$

$$A_{4-k}X_kF_{4+2k}, \quad 2.00 \leq k \leq 2.40 \quad \text{for } AXF_4.$$

The fluorine atoms in excess of eight per unit cell are probably distributed at random over the sites

$$\left(\frac{1}{2}, 0, 0\right), \left(0, \frac{1}{2}, 0\right), \left(0, 0, \frac{1}{2}\right), \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right).$$

3. Compounds isostructural with LaF₃

The cell dimensions given in Table 3 refer to the hexagonal pseudo-cell containing two metal atoms and six anions. This cell accounts for all the diffraction lines observed in powder patterns. The true unit cell is said to be three times as large (Ofstedal, 1931), i.e. the true a_1 axis is $\sqrt{3}$ times as large as indicated in Table 3.

Table 3. LaF₃ type

Compound	a_1 (kX.)	a_3 (kX.)
AcF ₃	4.27 ± 0.01	7.53 ± 0.02
UF ₃	4.138 ± 0.003	7.333 ± 0.004
NpF ₃	4.108 ± 0.001	7.273 ± 0.004
PuF ₃	4.087 ± 0.001	7.240 ± 0.001
AmF ₃ *	4.073 ± 0.002	7.231 ± 0.004
ThOF ₂	4.039 ± 0.002	7.290 ± 0.004
CaThF ₆	4.025 ± 0.010	7.175 ± 0.015
SrThF ₆	4.125 ± 0.005	7.327 ± 0.015
BaThF ₆	4.280 ± 0.005	7.520 ± 0.011
PbThF ₆	4.192 ± 0.003	7.395 ± 0.005
SrUF ₆	4.103 ± 0.005	7.290 ± 0.015
BaUF ₆	4.265 ± 0.005	7.456 ± 0.015
PbUF ₆	4.175 ± 0.005	7.337 ± 0.015

* Degree of purity uncertain.

In the 'pseudo-trifluorides' AXF₆ there is one stoichiometric molecule in the pseudo-cell, and the A atoms and X atoms seem to be randomly distributed over the metal sites.

4. Compounds isostructural with PbFCl

In the tetragonal PbFCl type of structure, containing two stoichiometric molecules per unit cell, the metal atoms are at positions $(\frac{1}{2}, 0, u)$, $(0, \frac{1}{2}, \bar{u})$, the smaller anions at $(0, 0, 0)$, $(\frac{1}{2}, \frac{1}{2}, 0)$ and the larger anions at $(\frac{1}{2}, 0, v)$, $(0, \frac{1}{2}, \bar{v})$.

Table 4 gives the unit-cell dimensions and the experimentally determined values of the parameters u and v .

Table 4. PbFCl type

Compound	a_1 (kX.)	a_3 (kX.)	u	v
AcOCl	4.24 ± 0.02	7.07 ± 0.03	—	—
AcOBr	4.27 ± 0.02	7.40 ± 0.03	—	—
PuOCl	4.004 ± 0.002	6.779 ± 0.010	0.18	0.64
PuOBr	4.014 ± 0.004	7.556 ± 0.011	0.16	0.64
PuOI	4.034 ± 0.002	9.151 ± 0.015	0.13	0.67
PrOCl	4.045 ± 0.003	6.786 ± 0.009	0.18	0.64
NdOCl	4.03 ± 0.03	6.76 ± 0.04	0.18	0.64
NdOBr	4.009 ± 0.006	7.604 ± 0.020	0.16	0.64
YOCl	3.892 ± 0.002	6.591 ± 0.004	0.18	0.64

Table 5. ZrF₄ type

Compound	a_1 (kX.)	a_2 (kX.)	a_3 (kX.)	α_2
ZrF ₄	11.69	9.87	7.64	126° 9'
HfF ₄	11.68	9.84	7.62	126° 5'
ThF ₄	13.1 ± 0.1	11.0 ± 0.1	8.6 ± 0.1	126° ± 1°
UF ₄	12.79 ± 0.06	10.72 ± 0.05	8.39 ± 0.05	126° 10' ± 30'
NpF ₄	12.67 ± 0.06	10.62 ± 0.05	8.31 ± 0.05	126° 10' ± 30'
PuF ₄	12.59 ± 0.06	10.55 ± 0.05	8.26 ± 0.05	126° 10' ± 30'
CeF ₄	12.6 ± 0.1	10.6 ± 0.1	8.3 ± 0.1	126° ± 1°

5. Compounds isostructural with ZrF₄

Only unit-cell dimensions and space group have been reported for ZrF₄ and HfF₄ (Schulze, 1934). The compounds are monoclinic with twelve stoichiometric molecules per unit cell. The space group is given as C_{2h}^6 . The choice of axes corresponds to a body-centered translation group. (The Mauguin-Hermann symbol $C2/c$ given in *Strukturbericht*, 3, 328, clearly is not appropriate when a body-centered translation group is used.)

The unit-cell dimensions given in Table 5 refer to a base-centered translation group and space group setting $C2/c$. The relationship between Schulze's axes a'_1, a'_3 and those of Table 5 are $a_1 = -a'_1 - a'_3$ and $a_3 = a'_3$.

The fluorine positions are unknown. The positions of the uranium atoms in UF₄ are:

$$4 U_I \text{ in } \pm(0, u, \frac{1}{4}) \text{ with } u=0.200,$$

$$8 U_{II} \text{ in } \pm(x, y, z), (x, \bar{y}, z + \frac{1}{2})$$

with $x=0.208$, $y=0.437$ and $z \approx -0.17$.

6. Compounds isostructural with La₂O₃

Ac₂O₃ and Th₂N₃ are the only new compounds with the La₂O₃ type of structure. The dimensions of the hexagonal unit cell containing one stoichiometric molecule are:

	a_1 (kX.)	a_3 (kX.)
Ac ₂ O ₃	4.07 ± 0.01	6.29 ± 0.02
Th ₂ N ₃	3.875 ± 0.002	6.175 ± 0.004

The metal atoms are at $\pm(\frac{1}{3}, \frac{2}{3}, u)$. One anion is at $(0, 0, 0)$ and two at $\pm(\frac{1}{3}, \frac{2}{3}, v)$. The parameter values $u=0.235$ and $v=0.63$ given by Pauling (1928) for La₂O₃ give average distances Ac-O=2.61 Å. and Th-N=2.51 Å.

7. Compounds isostructural with sodium uranyl acetate

Sodium neptunyl acetate and sodium plutonyl acetate are cubic and isostructural with the analogous uranyl compound (Fankuchen, 1935). The unit-cell constants are:

$$\text{Neptunyl compound: } a = 10.659 \pm 0.002 \text{ kX.}$$

$$\text{Plutonyl compound: } a = 10.643 \pm 0.002 \text{ kX.}$$

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:

$$\begin{aligned} Ce-12 Pt &= 3.198 \text{ kX.}, & Ce-4 Ce &= 3.340 \text{ kX.}, \\ Pt-6 Pt &= 2.727 \text{ kX.} & \text{and } Pt-6 Ce &= 3.198 \text{ kX.} \end{aligned}$$

10. Compound isostructural with $CaTiO_3$

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

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

11. Compound isostructural with UO_2F_2

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

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

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 $LaPO_4$

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

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

13. Compound isostructural with UCl_4

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

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

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

$$Np-4 Cl = 2.61 \text{ \AA.} \quad \text{and} \quad Np-4 Cl = 2.86 \text{ \AA.}$$

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 ₂ S ₃	Th ₂ S ₃ , U ₂ S ₃ , Np ₂ S 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 ₃ P ₄	Ac ₂ S ₃ , Pu ₂ S ₃ , Am ₂ S ₃	VI
	La ₂ S ₃ , Ce ₂ S ₃ -Ce ₃ S ₄	VI
K ₂ GeF ₆	Cs ₂ FuCl ₆	II

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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.

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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 $U-9F = 2.31$ \AA. 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 $Na-6F = 2.34$ \AA. and $Th-9F = 2.40$ \AA.

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