not distinguishable as long as the crystal is smaller than c. 270 A.

Although the present theory disregards the effects of inelastic scattering, it may be useful to interpret the fine structure and anomalous intensity observed in the electron-diffraction patterns, and it may serve also for a better understanding of results observed in electron micrographs and diffraction patterns of convergent electron beams (e.g. Heidenreich, 1942).

We hope soon to give elsewhere a more detailed derivation of the formulae, together with the interpretation of the results and some numerical examples.

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Crystal Chemical Studies of the 5*f*-Series of Elements. XIV. Oxyfluorides, *X*OF

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The hydrolysis of LaF_3 and YF_3 has been studied, and isolated preparations of AcOF and PuOF have been examined. LaOF and YOF have been prepared in two forms, one being rhombohedral and the other tetragonal. The crystal structures of both forms have been determined and are shown to be superstructures based upon the fluorite type.

PuOF is shown to have the tetragonal structure. The single investigated sample of AcOF appears to be truly cubic with the fluorite structure.

This paper gives the results of a structural study of oxyfluorides *X*OF, where *X* represents a 5*f*-element, a 4*f*-element or yttrium. The specific compounds which have been investigated are AcOF, PuOF, LaOF and YOF. Yttrium was used as a crystal chemical stand-in for elements at the end of the 4*f*-series. Since LaOF and YOF have been found to be isostructural, it may be safely assumed that oxyfluorides *X*OF of all 4*f*-elements will be structurally analogous. The fact that AcOF and YOF are isostructural, actinium being the largest of the trivalent 5*f*-elements, makes it possible to predict with assurance that oxyfluorides *X*OF of all 5*f*-elements will belong to the same isostructural series of compounds.

The preparations of PuOF and AcOF

PuOF

In early 1944 J. Karle tried to prepare plutonium metal by atomic hydrogen reduction of plutonium tetrafluoride. The reduction was carried out on the 20 μg. scale. The reaction product was submitted to me for identification and X-ray diffraction study.

The diffraction pattern showed the preparation to contain about 10% of PuF_3. The bulk of the sample was found to consist of a cubic face-centered phase with $a = 5{\cdot}70 \pm 0{\cdot}01$ A. A few very weak diffraction lines corresponded neither to PuF_3 nor to the cubic phase. It was at the time assumed that these diffraction lines were due to a small amount of impurity.

On the basis of the method of preparation the cubic phase would have to be plutonium metal, a plutonium fluoride, an oxyfluoride or an oxide. (In preparations on the microgram scale the possible presence of oxygen must always be considered.) At the time X-ray diffraction investigations had led to conclusive identification of plutonium metal and of the following oxides and fluorides: PuO_2, Pu_4O_7, PuO, PuF_4 and PuF_3. The cubic face-centered phase found in Karle's preparation corresponded to none of the previously identified compounds.

On the basis of extensive experimental data I had shown that the volume required by an oxygen or a fluorine atom in compounds of the heavy elements is about 19 $A.^3$, and that the volume requirement of the heavy cation could be neglected in the first approximation. Since the unit-cell volume of the cubic phase is 185 $A.^3$, eight oxygen plus fluorine atoms per unit cell were strongly indicated. The observed intensities required four plutonium atoms in the unit cell and a fluorite type of structure.

Thus the two possible chemical formulas for the unknown cubic phase were found to be PuF_2 or PuOF. The cation–anion distance of 2·47 A. favored the formula PuOF. However, too little was known about the chemistry and crystal chemistry of plutonium at that time to justify a reliable decision between the two formulas on the basis of interionic distances.

Subsequent direct chemical analysis showed conclusively that the cubic phase is PuOF.

Recently I have shown, as will be discussed in later sections of this paper, that LaOF is not cubic as previously supposed but rather tetragonal or rhombohedral. In view of these new results I have re-examined the old diffraction data for PuOF. It was mentioned above that the diffraction pattern of PuOF contained a few weak lines which could not be accounted for. The re-examination of the data show that these weak diffraction lines all correspond to a tetragonal superstructure analogous to the one observed for LaOF. Thus the investigated preparation of PuOF is tetragonal pseudo-cubic rather than cubic.

AcOF

AcF_3 was one of the very first actinium compounds to be prepared and identified. Sherman Fried and F. Hagemann tried to prepare AcOF by hydrolysis from the trifluoride preparation. After several unsuccessful attempts (the X-ray diffraction patterns showing unreacted AcF_3) the hydrolysis was found to take place at 1200° C. The preparation was carried out with about 10 μg. of material.

Because of γ radiation from actinium daughters it is difficult to obtain measurable X-ray diffraction patterns of actinium preparations on the 5–10 μg. scale. It is necessary to take the diffraction data within a few hours after the initial separation of actinium from its daughters. Even with such precautions the X-ray patterns have a heavy background due to γ radiation.

The diffraction pattern of the hydrolyzed actinium fluoride preparation mentioned above showed the sample to contain about 85% of a cubic face-centered phase with $a = 5{\cdot}932 \pm 0{\cdot}002$ kX. The observed intensities require a fluorite type of structure. AcOF is the only chemical formula compatible with the data and the trivalency of actinium.

The sample contained about 15% of a second, as yet unidentified, phase.

Superstructure lines, showing that AcOF is only pseudo-cubic, were not observed. It should be remarked, however, that such superstructure lines may be present, but are not visible because of the heavy background due to the γ radiation.

The system LaF_3–La_2O_3

When LaF_3 is kept at a temperature of about 900° C. in an atmosphere of low humidity it slowly loses weight because of hydrolysis. The hydrolysis proceeds until the fluoride is completely converted to oxide according to the equation: $2LaF_3 + 3H_2O = La_2O_3 + 6HF$.

This slow hydrolysis offered a convenient way for studying the system LaF_3–La_2O_3. Lanthanum fluoride of high purity supplied by the City Chemical Company served as starting material. X-ray diffraction patterns showed only the lines of anhydrous LaF_3. Complete conversion to lanthanum oxide involved a weight loss of 18·5%, as compared with the theoretical value of 16·9%. It is believed that the difference of 1·6% represents adsorbed moisture.

The progress of the hydrolysis was followed by means of frequent X-ray diffraction patterns and weighings. The effective molecular weight, M, per lanthanum atom of the partially hydrolyzed fluoride was determined from the weight of the sample, and the X-ray diffraction patterns gave the phase composition. The results of these measurements are shown in Table 1.

Table 1. *Hydrolysis of* LaF_3

Heat treatment	M	Phase composition
Initial sample	200	LaF_3
2 hr. at 920° C.	182	Tetragonal LaOF
3½ hr. at 920° C.	177	Tetragonal LaOF
5½ hr. at 920° C.	174	Tetragonal LaOF
10½ hr. at 920° C.	172	Rhombohedral LaOF
31 hr. at 920° C.	170	Rhombohedral LaOF + La_2O_3
31 hr. at 920° C. and 19 hr. at 1130° C.	(163)	La_2O_3

As shown in Table 1 there are two lanthanum oxyfluoride phases. According to the interpretation of the X-ray diffraction patterns, one phase is tetragonal and the other rhombohedral.

The tetragonal phase has a wide homogeneity range extending from 40 mole % LaF_3, 60 mole % LaOF, to 100% LaOF. The unit-cell dimensions decrease with increasing oxygen content.

The chemical composition of the rhombohedral phase is sharply defined and corresponds to the exact formula LaOF. No variation in unit-cell dimensions of this phase is observed.

The system LaF_3–La_2O_3 was studied some years ago by Klemm & Klein (1941). These workers made the oxyfluoride preparations by heat treating in vacuum weighed amounts of LaF_3 and La_2O_3. My results agree with those of Klemm & Klein as to the existence of two phases and as to homogeneity ranges for the two phases. However, the phase with the wide homogeneity range which I found to be tetragonal is reported as cubic by Klemm & Klein. According to the earlier work the second phase is 'probably tetragonal', whereas I found it to be rhombohedral.

The system YF_3–Y_2O_3

This system was investigated by the same method as described for the system LaF_3–La_2O_3.

The anhydrous yttrium fluoride used as starting material I prepared by precipitating a yttrium nitrate solution with hydrogen fluoride. The precipitate was carefully washed and dried for 24 hr. at 130° C.

The hydrolysis of yttrium fluoride in the room atmosphere was found to proceed at a suitable rate at a temperature of 500° C. The data obtained are given in Table 2.

The results for the system YF_3–Y_2O_3 are strictly analogous to the findings for the corresponding lanthanum system. The homogeneity range for the tetragonal phase extends from the ideal composition YOF to 60 mole % YOF, 40 mole % YF_3. The rhombohedral phase corresponds to the exact composition YOF.

Table 2. *Hydrolysis of* YF_3

Heat treatment	M	Phase composition
Initial sample	148	YF_3
24 hr. at 400° C.	137	YF_3 + tetragonal YOF
48 hr. at 500° C.	126	Tetragonal YOF
72 hr. at 500° C.	124	Rhombohedral YOF and tetragonal YOF
96 hr. at 500° C.	123	Rhombohedral YOF
and 48 hr. at 900° C.	(113)	Y_2O_3

On the X-ray diffraction data

All X-ray diffraction data to be discussed in this paper are taken with Cu K radiation filtered through nickel foil. The samples were all in finely divided form. Single crystals were not discernible, even in a high-power microscope.

The X-ray diffraction patterns of PuOF and AcOF are not very good because only very small amounts of material were available. The preparations of YOF were not sufficiently well crystallized to give sharp diffraction lines in the back-reflection region. The diffraction patterns of LaOF were of excellent quality. In some of the LaOF patterns, the α_1 and α_2 components are well separated at glancing angles of 30°.

The diffraction patterns of the rhombohedral as well as the tetragonal phase resemble that of a fluorite type of structure. This resemblance is most striking for the tetragonal phase. The strong lines in the patterns of the rhombohedral and tetragonal phases correspond to cubic face-centered diffraction lines. Table 3 gives the indices of corresponding diffraction lines. In patterns of high resolution, such as the LaOF patterns, it is usually possible to measure separately each component of the pseudo-cubic lines. In addition to the pseudo-cubic lines the patterns of the rhombohedral and tetragonal phases show a considerable number of superstructure lines. At small scattering angles the superstructure lines are very weak and may easily be overlooked or be presumed to be due to small impurities.

Table 3. *Corresponding reflections*

ΣH_i^2	Cubic $H_1H_2H_3$	Tetragonal $H_1H_2H_3$	Rhombohedral $H_1H_2H_3$
3	111	101	110, 222
4	200	110, 002	211
8	220	200, 112	$10\bar{1}$, 332
11	311	103, 211	200, 321, 433
12	222	202	220, 444
16	400	220, 004	422
19	331	301, 213	$21\bar{1}$, 442, 554
20	420	310, 222	310, 543
24	422	312, 204	$2\bar{1}\bar{1}$, 431, 655
27	511, 333	321, 105, 303	411, 330, 532, 644, 666
32	440	400, 224	$20\bar{2}$, 664
35	531	411, 323, 215	$30\bar{1}$, 420, 653, 765
36	600, 442	330, 006, 402, 314	$32\bar{1}$, 633, 552, 776
40	620	420, 332, 116	521, 754

The crystal structure of the rhombohedral phase XOF

Tables 4 and 5 give the diffraction data up to $\sin^2\theta = 0{\cdot}500$ for the rhombohedral forms of LaOF and YOF. The diffraction data from the back-reflection region for LaOF are shown in Table 6. The intensities listed in Table 4 were measured with a Geiger–Müller tube, while the observations of Tables 5 and 6 were obtained from photographs.

The observed sine squares require rhombohedral unit cells with the following dimensions

	a	α
LaOF	7·118 ± 0·001 kX. (7·132 ± 0·001 A.)	33·01 ± 0·01°
YOF	6·684 ± 0·005 kX. (6·697 ± 0·005 A.)	33·20 ± 0·02°

The unit cell contains two molecules XOF giving calculated densities of $\rho = 6{\cdot}020$ g.cm.$^{-3}$ for LaOF and $\rho = 5{\cdot}13$ g.cm.$^{-3}$ for YOF.

Table 4. *Powder spectrometer data for rhombohedral* LaOF

$H_1H_2H_3$	$\sin^2\theta$ Calc.	$\sin^2\theta$ Obs.	Intensity obs.
111	0·0131	0·0130	3
100	0·0496	—	0
222	0·0523	0·0525	45
110	0·0540	0·0541	112
211	0·0714	0·0714	35
221	0·0845	0·0847	5
333	0·1176	0·1181	5
322	0·1194	0·1196	6
332	0·1411	0·1414	51
$10\bar{1}$	0·1445	0·1446	64
210	0·1576	0·1577	1
433	0·1934	0·1937	18
$11\bar{1}$	0·1941		
321	0·1968	0·1970*	43
200	0·1984		
444	0·2091	0·2095	3
220	0·2158	0·2161	11
443	0·2239	0·2242	4
311	0·2289	0·2291	2
432	0·2621	0·2625	6
331	0·2638	0·2637	5
422	0·2855	0·2857	12
544	0·2936	0·2938	4
555	0·3267	0·3269	2
554	0·3328	0·3331	5
442	0·3378	0·3382	8
$20\bar{1}$	0·3386	—	0
$21\bar{1}$	0·3429	0·3433	17
543	0·3536	0·3538	7
310	0·3603	0·3608	9
533	0·3683	0·3682	2
320	0·3734	0·3740	1
421	0·4083	0·4089	2
655	0·4200	0·4204	4
431	0·4300	0·4304	14
$2\bar{1}\bar{1}$	0·4334	0·4337	11
553	0·4380	—	0
300, $22\bar{1}$	0·4465	—	0
665	0·4679	0·4686	3
666	0·4705	0·4712	6
654	0·4712		
644	0·4772	0·4775	3
532	0·4823	0·4829	8
411, 330	0·4857	0·4859	10

* Broad reflection.

Table 5. *Diffraction data for rhombohedral* YOF

$H_1H_2H_3$	$\sin^2\theta$ Calc.	$\sin^2\theta$ Obs.	Intensity obs.
111	0·0149	—	Nil
100	0·0559	—	Nil
222	0·0595	0·0622	*vs*
110	0·0608		
211	0·0806	0·0828	*w*+
221	0·0955	0·0974	*vvw*
333	0·1339	0·1367	*vw*
322	0·1352		
332	0·1600	0·1640	*s*+ (diffuse)
$10\bar{1}$	0·1625		
210	0·1774	—	Nil
$11\bar{1}$	0·2183	—	Nil
433	0·2195	0·2252	*s* (diffuse)
321	0·2220		
200	0·2232		
444	0·2380	—	Nil
220	0·2430	0·2464	*vw*+
443	0·2542	0·2565	*vvw*
311	0·2579	—	Nil
432	0·2964	0·3002	*vw*
331	0·2976		
422	0·3224	0·3259	*w*+
544	0·3336	0·3357	*vw*−
555	0·3719	—	Nil
554	0·3782	0·3835	*vw*
$20\bar{1}$	0·3808		
442	0·3819		
$21\bar{1}$	0·3857	0·3894	*m*+
543	0·4005	0·4036	*vw*+
310	0·4055	0·4084	*w*
533	0·4166	—	Nil
320	0·4204	—	Nil
421	0·4601	0·4644	Trace
655	0·4774	0·4791	*vvw*+
431	0·4849	0·4894	*ms*
$2\bar{1}\bar{1}$	0·4874		
553	0·4960	—	Nil

The observed intensities show that the structure factor depends upon the indices $H_1H_2H_3$ only in the linear combination $H_1+H_2+H_3$. Accordingly all atoms are situated on the threefold axis. It will be assumed that the structure has an inversion center. This assumption is proved to be correct by the agreement attained between observed and calculated intensities.

Thus the proposed structure is:

$$2X \text{ in } \pm(u, u, u),\ 2\text{F in } \pm(v, v, v),\ 2\text{O in } \pm(w, w, w).$$

The space group symmetry is $R\bar{3}m$.

A cursory inspection of the observed intensities shows $u \doteqdot \frac{1}{4}$, $v \doteqdot \frac{1}{8}$ (or $\frac{3}{8}$), $w \doteqdot \frac{3}{8}$ (or $\frac{1}{8}$).

The back-reflection data for LaOF permit a fairly accurate determination of the parameter u. Values for v and w have been chosen so as to make each fluorine atom or each oxygen atom equidistant from the four nearest metal atoms. It is believed that the values for v and w so obtained are more accurate than could be obtained from intensity calculations alone.

The parameter values for LaOF are:

$$u = 0{\cdot}242 \pm 0{\cdot}001,\ v = 0{\cdot}122 \text{ (or } 0{\cdot}370),$$
$$w = 0{\cdot}370 \text{ (or } 0{\cdot}122).$$

The same parameter values seem to apply also to YOF.

It is not possible by means of intensity calculations to distinguish between oxygen and fluorine atoms. However, it is invariably observed that metal–fluorine distances are shorter than corresponding metal–oxygen distances. On this basis the alternative values of v and w given in parentheses above have to be rejected.

The calculated intensities listed in Table 6 were obtained using the formula

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

where p is the permutation factor.

The interatomic distances are:

$$\text{La–4F} = 2{\cdot}42 \text{ A.} \quad \text{La–4O} = 2{\cdot}58 \text{ A.}$$
$$\text{Y –4F} = 2{\cdot}28 \text{ A.} \quad \text{Y –4O} = 2{\cdot}44 \text{ A.}$$

The structure should be regarded as a superstructure derived from the fluorite type. A fluorite structure with $a = 5{\cdot}754$ kX. can be referred to a rhombohedral cell with $\alpha = 33{\cdot}22°$ and the same volume as observed for rhombohedral LaOF. The atomic positions of cations and anions in this rhombohedron are the same as found for LaOF except that $u = 0{\cdot}250$, $v = 0{\cdot}125$, $w = 0{\cdot}375$.

Table 6. *Back-reflection data for rhombohedral* LaOF

$H_1H_2H_3$	$\sin^2\theta$ Calc.	$\sin^2\theta$ Obs.	Intensity Calc.	Intensity Obs.
877	0·7511	0·7518	3·9	10
764	0·7568	0·7575	37·6	40
744, 663, α_2 764	0·7601	0·7613	49·4	60
541	0·7712	0·7720	43·5	60
$3\bar{1}\bar{1}$	0·7720	—	0·1	0
866	0·7735	—	3·9	0
$22\bar{2}$, α_2 541	0·7763	0·7770	49·8	60
876	0·7849	0·7855	40·6	50
642, α_2 876	0·7870	0·7884	47·0	50
400	0·7937	0·7952	20·7	20
632	0·8017	0·8026	16·2	20
$33\bar{1}$	0·8068	—	1·9	0
887	0·8164	0·8174	30·0	50
888	0·8365	0·8372	2·0	5
511	0·8417	0·8433	4·6	5
865	0·8613	0·8617	45·9	50
440	0·8634	0·8646	39·7	50
652	0·8714	0·8722	26·3	25
886	0·8955	0·8961	6·2	10
855, 774	0·9039	0·9048	31·7	80
753	0·9046		47·2	
743	0·9106	0·9111	47·6	55
622, α_2 743	0·9157	0·9163	58·8	60
$30\bar{2}$	0·9165	—	0·3	0
875	0·9180	0·9187	13·0	10
$31\bar{2}$, α_2 622	0·9208	0·9216	115·0	130
$41\bar{1}$	0·9382	0·9391	74·5	100
551	0·9462	0·9465	16·0	10
$42\bar{1}$	0·9513	0·9519	7·3	10
988	0·9558	0·9559	68·9	75
977, α_2 988	0·9608	0·9609	99·4	120
987	0·9810	0·9811	35·5	50
520	0·9862	0·9864	34·0	55

The formation of the rhombohedral superstructure XOF is clearly associated with the ordering of oxygen and fluorine atoms into distinct sites. Numerous samples of rhombohedral LaOF have been prepared, but not the slightest variation in unit-cell dimensions or diffraction intensities has been observed. This fact suggests that there is complete order in the structure.

The X–O distance is 0·16 A. greater than the X–F distance as compared with a difference of −0·01 A. predicted from the Goldschmidt ionic radii and of 0·04 A. predicted from the Pauling ionic radii. Such discrepancies between observed and predicted X–O and X–F distances occur quite universally when X is an inert-gas-shell ion of valence three or less, and suggest that the Goldschmidt–Pauling ionic radii are in need of revision.

The crystal structure of the tetragonal phase XOF

As mentioned earlier in this paper, the tetragonal phase has been observed for LaOF, YOF and PuOF. The homogeneity range of this phase is wide, and the unit-cell dimensions decrease with decreasing fluorine content.

Some of the diffraction data for the tetragonal oxyfluorides are listed in Tables 7–10. The observed sine squares correspond to a tetragonal unit cell with $a_3/a_1 \doteqdot \sqrt{2}$ and containing two metal atoms. The chemical composition of the phase throughout its homogeneity range can be expressed by the formula

$$XO_nF_{3-2n},\ 0{\cdot}7 < n < 1{\cdot}0.$$

The tetragonal phase is stabilized by the presence of excess fluorine over the ideal composition XOF. When $n = 1{\cdot}0$ the tetragonal phase is unstable relative to the rhombohedral phase.

Table 7. *Powder spectrometer data for tetragonal* LaOF

	$\sin^2\theta$		
$H_1H_2H_3$	Calc.	Obs.	Intensity obs.
001	0·0174	0·0173	2
101	0·0528	0·0527	110
002	0·0695	0·0694	15
110	0·0708	0·0706	28
111	0·0882	0·0880	3
102	0·1049	0·1049	15
112	0·1403	0·1403	66
200	0·1416	0·1418	36
003	0·1563	0·1565	3
201	0·1590	0·1589	2
103	0·1917	0·1922	24
211	0·1944	0·1944	48
202	0·2111	0·2112	14
113	0·2271	0·2271	6
212	0·2465	0·2470	5
004	0·2779	0·2780	4
220	0·2833	0·2835	9
203	0·2979	0·2982	3
221	0·3007	—	—
104	0·3133	0·3137	6
213	0·3333	0·3333	14
301	0·3361	0·3352	13
114	0·3487	0·3488	3
222	0·3528	0·3538	10
310	0·3541		
311	0·3715	0·3719	1
302	0·3882	0·3884	1
204	0·4195	0·4199	6
312	0·4236	0·4235	15
005	0·4342	0·4342	2
223	0·4396	0·4401	2
214	0·4549	0·4549	4
105	0·4696	0·4697	3
303	0·4750	0·4752	4
321	0·4777	0·4778	11

Table 8. *Diffraction data for tetragonal* YOF

	$\sin^2\theta$		
$H_1H_2H_3$	Calc.	Obs.	Intensity
001	0·0201	0·0203	Trace
101	0·0589	0·0599	*vs*
110	0·0776	0·0785	*w*+
002	0·0806	0·0812	*vvw*
111	0·0977	—	Nil
102	0·1194	0·1198	*w*
200	0·1552	0·1568	*m*−
112	0·1582	0·1587	*s*−
201	0·1753	0·1758	*vvw*
003	0·1813	0·1830	*vvw*−
211	0·2143	0·2154	*s*
103	0·2201	0·2210	*w*
202	0·2358	0·2368	*w*
113	0·2589	0·2593	*w*
212	0·2746	0·2755	*w*−
220	0·3104	0·3119	*w*
004	0·3222	0·3238	*vvw*
221	0·3305	—	Nil
203	0·3365	0·3369	*w*−
104	0·3610	0·3595	*w*−
301	0·3693	0·3698	*w*
213	0·3753	0·3750	*w*
310	0·3880	0·3896	*w*+
222	0·3910		
114	0·3998	—	Nil
311	0·4081	—	Nil
302	0·4298	0·4289	Trace
312	0·4686	0·4686	*m*
204	0·4774	0·4765	*vvw*
005	0·5035	0·5035	*vw*−
214	0·5162	0·5157	*w*+
321	0·5245	0·5251	*w*+ (diffuse)
303	0·5305	—	—

Table 9. *Diffraction data for* PuOF

	$\sin^2\theta$		
$H_1H_2H_3$	Calc.	Obs.	Intensity
101	0·0548	0·0553	*vs*
110, 002	0·0730	0·0741	*m*
102	0·1095	0·1110	*vw*
112, 200	0·1461	0·1476	*s*
201, 003	0·1643	0·1649	*vw*
103, 211	0·2009	0·2029	*s*
222	0·2191	0·2206	*w*−
113	0·2373	0·2373	*vvw*
220, 004	0·2922	0·2942	*w*−
301, 213	0·3469	0·3463	*m*−
310, 222, 114	0·3652	0·3664	*w*.
312, 204	0·4382	0·4379	*m*−
321, 303, 105	0·4930	0·4946	*w*
313, 115	0·5295	0·5276	*vw*−
400, 224	0·5843	0·5808	*vw*
411, 323, 215	0·6391	0·6390	*w*−
330, 402, 314, 006	0·6574	0·6575	*w*−

Unit-cell dimensions are as follows:

	n	a_1 (kX.)	a_3 (kX.)
LaOF	1·0	4·083 ± 0·001	5·825 ± 0·001
	0·7	4·098 ± 0·002	5·840 ± 0·004
YOF	1·0	3·910 ± 0·005	5·431 ± 0·01
	0·7	3·930 ± 0·005	5·46 ± 0·01
PuOF	~1·0	4·04 ± 0·01	5·71 ± 0·01

The observed intensities require the atomic positions for the ideal composition XOF to be

$$2X \text{ in } (\tfrac{1}{2}, 0, u),\ (0, \tfrac{1}{2}, \bar{u});$$
$$2\mathrm{F} \text{ in } (0, 0, 0),\ (\tfrac{1}{2}, \tfrac{1}{2}, 0);$$
$$2\mathrm{O} \text{ in } (0, 0, \tfrac{1}{2}),\ (\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}).$$

Table 10. *Back-reflection data for tetragonal* LaOF

$H_1H_2H_3$	$\sin^2\theta$ Calc.	$\sin^2\theta$ Obs.	Intensity Calc.	Intensity Obs.
305	0·7545	0·7550	23	20
413, α_2 305	0·7594	0·7599	90	90
206	0·7688	—	7	0
422	0·7787	0·7793	70	80
315	0·7899	0·7901	70	70
333, α_2 315	0·7948	0·7947	36	50
216	0·8043	0·8042	90	100
404	0·8459	0·8463	56	50
007	0·8534	0·8534	16	15
423	0·8657	0·8662	36	50
414	0·8814	0·8815	63	70
107	0·8889	—	8	0
325	0·8963	0·8965	67	50
501, 431	0·9037	0·9041	256	200
226	0·9106	—	12	0
334	0·9168	0·9170	37	35
510, α_2 334	0·9217	0·9220	81	60
117	0·9243	0·9242	84	60
511	0·9391	—	8	0
306	0·9461	0·9461	87	70
502, 432	0·9560	0·9563	45	60

Using the back-reflection intensity data for LaOF, the parameter value is found to be $u = 0{\cdot}222 \pm 0{\cdot}004$. The same value of u seems to be valid also for YOF and PuOF. (The value $u = 0{\cdot}278$ gives equally good agreement with observed intensities, but must be rejected because it makes the La–O distance shorter than the La–F distances.)

The interionic distances are

La–4O = 2·61 A. La–4F = 2·42 A.
Y –4O = 2·47 A. Y –4F = 2·30 A.
Pu–4O = 2·57 A. Pu–4F = 2·39 A.

The tetragonal XOF structure is, as was true of the rhombohedral structure, a superstructure based upon the fluorite type. If the fluorite structure is referred to a tetragonal cell with two molecules and an axial ratio $a_3/a_1 = \sqrt{2}$, the cation and anion positions would be the same as for the tetragonal XOF structure except that $u = \frac{1}{4}$. The superstructure formation is, as in the rhombohedral form, to be attributed to the segregation of oxygen and fluorine atoms into distinct sets of lattice sites.

At the fluorine-rich end of the homogeneity range the chemical composition is $XO_{0.7}F_{1.6}$ and the unit cell contains two such 'molecules'. Thus the unit cell contains more than four anions. The only reasonable positions for the interstitial anions are $(\frac{1}{2}, 0, v)$, $(0, \frac{1}{2}, \bar{v})$, with $v \doteq \frac{3}{4}$.

In diffraction patterns of samples with excess fluorine the intensity of the superstructure lines is decreased relative to the values observed for the ideal composition XOF. In other words the parameter value u increases with increasing fluorine content.

The atomic positions at the fluorine-rich end of the homogeneity range appear to be

2X in $(\frac{1}{2}, 0, u)$, $(0, \frac{1}{2}, \bar{u})$, with $u = 0{\cdot}235$;
2F in $(0, 0, 0)$, $(\frac{1}{2}, \frac{1}{2}, 0)$;
1·4O + 0·6F in $(0, 0, \frac{1}{2})$, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$;
0·6O in $(\frac{1}{2}, 0, v)$, $(0, \frac{1}{2}, \bar{v})$, with $v \doteq \frac{3}{4}$.

The crystal structure of the cubic phase XOF

The cubic phase has been observed only for AcOF, the diffraction data for which are given in Table 11. It should be emphasized that AcOF may be only pseudocubic, but there is no evidence of departure from cubic symmetry in the form of superstructure lines or splitting of lines.

Table 11. *Diffraction data for* AcOF

ΣH_i^2	$\sin^2\theta$	Intensity
3	0·0510	*vs*
4	0·0685	*m*
8	0·1360	*s*
11	0·1862	*s*
12	0·2023	*w*
16	0·2701	*w*
19	0·3213	*ms*
20	0·3374	*m*–
24	0·4055	*m*
27	0·4557	*m*
32	0·5389	*vw*
35	0·5891	*m*
36	0·6070	*w*–
40	0·6736	*w*+
43	0·7251	*w*
44	0·7412	*w*–
48	0·8088	*vw*–
51 α_1	0·8564	*ms*
52 α_1	0·8723	*w*–
56 α_1	0·9407	*s*

The cubic form has the fluorite type of structure, the oxygen and fluorine atoms being statistically distributed over the eightfold anion sites. The unit-cell constant is $a = 5{\cdot}931 \pm 0{\cdot}002$ kX., corresponding to a calculated density of 8·28 g.cm.$^{-3}$ and an interionic distance Ac–8 (O, F) = 2·57 A. It is possible that there is excess fluorine over the formula AcOF. In such a case there would be some interstitial anions in the sites $(\frac{1}{2}, 0, 0)$, $(0, \frac{1}{2}, 0)$, $(0, 0, \frac{1}{2})$, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.

All efforts to prepare truly cubic samples of LaOF and YOF by quenching from high temperatures were unsuccessful. It proved possible by quenching to decrease the intensity of the tetragonal superstructure lines, thus indicating a smaller degree of order at higher temperatures. However, the superstructure lines could not be entirely suppressed. It is not unlikely that the cubic form does exist at high temperatures and that the failure of the attempts to prepare the cubic form by quenching is due to the difficulty of attaining sufficiently rapid cooling rates because of low thermal conductivity.

Valuable aid was given by Dr J. Karle who prepared the PuOF sample, by Drs Sherman Fried and French Hagemann who made the AcOF preparation, and by Miss A. Plettinger who took all the powder photographs.

Reference

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