cloudiness or precipitation of hydrated titanium dioxide observed. This inflection appears to signify some change in polymeric structure preceding the precipitation of hydrated titanium dioxide from titanium sulfate solutions.

In the economically important hydrolyses of titanium salt solutions to produce titanium dioxide, titanium chloride solutions yield rutile while sulfate solutions produce anatase. Since the titanium tetrachloride solutions do not suffer any change in reactivity with tartaric acid until precipitation occurs while the sulfate solutions undergo pronounced changes in reactivity prior to their precipitation it appears reasonable to suppose that this difference in behavior may be related in some way to the ultimate formation of different types of crystal structures. The cross-linkage of linear titanic acid polymers such as are illustrated in diagram II may produce a different type of crystal lattice from that built up directly from the monomeric hydrated titanium chloride complexes.

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[CONTRIBUTION FROM LOS ALAMOS SCIENTIFIC LABORATORY, UNIVERSITY OF CALIFORNIA AND UNIVERSITY OF CHICAGO]

Preparation, Identification and Crystal Structure of a Pentavalent Americium Compound, $KAmO_2F_2$[1]

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$KAmO_2F_2$, prepared by the addition of a saturated solution of KF to an acid solution of pentavalent americium, is rhombohedral, $R\bar{3}m$, with one molecule in a unit cell with $a = 6.78$ Å., $\alpha = 36.25°$. The atomic positions are: 1 Am in (0,0,0), 1 K in ($^1/_2$,$^1/_2$,$^1/_2$), 2 O in $\pm$ (u,u,u) with $u = 0.102$, 2 F in $\pm$ (v,v,v) with $v = 0.356$. The structure ($CaUO_2O_2$ type) contains radicals $[AmO_2]^+$ and is built up of layers $(AmO_2F_2)^-$ held together by potassium ions.

The preparation of double carbonates of alkali with pentavalent transuranic elements was recently described by Nigon, *et al.*[3] The crystal structure of the hexagonal double carbonates has been determined for the isostructural series: $KPuO_2CO_3$, $NH_4PuO_2CO_3$ and $RbAmO_2CO_3$.[4] The present paper gives the results of X-ray diffraction studies of the double fluorides.

Preparation of the Compounds.—The americium used in this study contained no impurities above the spectroscopic limit of detection.

$KAmO_2CO_3$ was prepared by OCl^- oxidation of Am(III) in K_2CO_3 solution[3,5]; $RbAmO_2CO_3$ was prepared by $S_2O_8^{--}$ oxidation of Am(III) in Rb_2CO_3 solution.[3]

The alkali Am(V) carbonate compounds were washed with dilute alkali carbonate solution to reduce alkali carbonate concentration to <0.1 M $CO_3^=$ and to remove other ions. The solids were then dissolved in dilute HNO_3 to give a solution of AmO_2^+ in <0.1 M H^+.

The solution, containing approximately 10–20 g./l. of AmO_2^+, was treated with an equal volume of saturated alkali fluoride. The white precipitate formed was allowed to stand for 5–10 minutes, washed three times with *ca.* 10 volumes of water per wash, and slurried into a capillary. The solid, containing ~30 micrograms of americium,[6] was centrifuged into the capillary tip and the supernatant removed by means of a smaller capillary inserted into the larger one. The solid was then washed once with acetone, air-dried, and sealed off preparatory to X-ray examination.

X-Ray Diffraction Data and Chemical Composition.—The investigation is based upon two different samples, one being a potassium–americium fluoride precipitate, and the other an analogous preparation made with rubidium instead of potassium. It was subsequently found that the commercially supplied rubidium salt which was used in making the latter sample contained considerable amounts of potassium.

The X-ray diffraction data obtained with CuKα radiation for the pure potassium preparation (Table I) can be ascribed to a single phase with a rhombohedral unit cell of dimensions[7]: $a = 6.78 \pm 0.01$ Å., $\alpha = 36.25 \pm 0.05°$. The second sample, the rubidium preparation made with appreciable potassium content, gave unit cell dimensions: $a = 7.03 \pm 0.01$ Å., $\alpha = 35.11 \pm 0.05°$. The sample was found to contain a small amount of rubidium silicofluoride and traces of an unknown phase. The considerable increase in cell dimensions of the second sample over the first is proof that the alkali atoms are constituents of the structure. In view of the impure nature of the second sample, the crystal structure determination is based upon the diffraction data of the pure potassium preparation.

According to the method of chemical preparation, the cation constituents of the structure are K^+ and Am(V). It is generally supposed, and indeed directly verified for the double carbonates,[3] that the pentavalent state of americium involves radicals $[AmO_2]^+$. The conceivable anion constituents other than the oxygen atoms of the possible radicals $[AmO_2]^+$ are fluoride and nitrate ions.

It has been amply demonstrated for compounds of the heavy elements that it is possible to assign fixed volume requirements to the various ions, V_i, so that the volume of the unit cell is given (usually to better than 5%) by the sum ΣV_i.[8] Small, highly charged cations like Am^{+5} and N^{+5} have negligible volume requirements, since they fit into the interstices between the anions; others have assigned

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[1] This work was sponsored by the U. S. Atomic Energy Commission.

[2] Consultant to Los Alamos Scientific Laboratory; present address, University of Chicago, Chicago, Illinois.

[3] J. P. Nigon, R. A. Penneman, E. Staritzky, T. K. Keenan and L. B. Asprey, *J. Phys. Chem.*, **58**, 403 (1954).

[4] F. H. Ellinger and W. H. Zachariasen, *ibid.*, **58**, 405 (1954).

[5] L. B. Werner and I. Perlman, THIS JOURNAL, **73**, 495 (1951).

[6] Excessive film blackening results from the γ-radiation of Am^{241} with larger amounts of sample.

[7] The hexagonal cell has dimensions $a_1 = 4.22$ Å. $a_3 = 18.99$ Å.

[8] See, for instance W. H. Zachariasen, THIS JOURNAL, **70**, 2147 (1948).

TABLE I

X-RAY DIFFRACTION DATA AND CALCULATED INTENSITIES

	Sin² θ		Calcd. intensity			
$H_1H_2H_3$	Obsd.	Calcd.	Am atoms	K + Am atoms	All atoms	Obsd. intensity
111	0.0148	0.0149	89	59	77	80
100	.0467	.0462	73	50	53	50
110	.0516	.0511	70	98	100	100
222	.0594	.0594	21	30	27	30
211	.0714	.0709	50	72	42	40
221	.0860	.0858	43	28	20	15
322	.1256	.1255	28	20	12	10
$10\bar{1}$	.1340	.1335	29	39	60	60
333		.1341	10	7	9	
210	.1492	.1484	51	36	42	60
332		.1501	25	34	42	
$11\bar{1}$	.1802	.1797	20	15	16	15
200	.1853	.1846	20	27	27	25
321	.1935	.1929	38	51	50	40
220	.2064	.2044	18	23	16	15 diffuse
433		.2095	17	23	23	
311	...	.2196	16	12	9	..
444	.2385	.2376	5	6	6	10 diffuse
443		.2441	14	10	12	
331	.2611	.2590	13	9	6	5
432	.2671	.2676	26	19	25	20
422	.2827	.2836	12	16	20	15
$20\bar{1}$	.3170	.3132	22	16	17	35 diffuse
$21\bar{1}$		.3181	22	29	28	
544	....	.3242	11	8	6	..
310	.3379	.3379	20	26	19	20
442		.3430	10	13	14	
320	.3547	.3528	20	15	11	10
554	.3700	.3685	10	13	12	20 diffuse
543		.3711	19	25	25	
555		.3717	3	2	3	
533		.3776	10	7	9	
421	.3919	.3925	17	13	9	10
$2\bar{1}\bar{1}$	.4004	.4005	9	12	17	15
300, $22\bar{1}$	.4156	.4154	17	12	14	35
431		.4171	17	22	27	
553	.4593	.4569	8	6	5	20
411, 330		.4599	15	22	20	

values as follows (Å.³); K^+(21), AmO_2^+(38), O^{-2}(19), F^-(18), NO_3^-(57).[9]

The volume of the unit cell is 98 Å.³. Accordingly the unit cell contains a total of five atoms, at least one is a potassium atom and one an americium atom. A unit cell content corresponding to the formula $KAmO_2F_2$ is the only way of balancing valences subject to the necessary boundary conditions deduced from volume considerations. The presence of two oxygen atoms per americium atom strongly suggests the existence of radicals $[AmO_2]^+$ as previously observed in $Rb[AmO_2]CO_3$.

It should be emphasized that a consideration of diffraction intensities independently leads to the conclusion of one potassium atom and one americium atom per unit cell.

The chemical identity of the phase having been established, the density is calculated to be $\rho = 5.96$ g./cm.³

Determination of the Structure.—Since there is only one americium atom in the rhombohedral cell, the coördinate origin is conveniently laid in this atom, *i.e.*, 1 Am in (0,0,0). The intensity distribution is predominantly determined by the strongly scattering americium atom, but the effect of the other atoms is readily discernible. This is seen from Table I where column 7 gives the observed intensities and column 4 those calculated on the basis of the americium contribution alone. Reflections with odd values of ΣH_i appear much weaker and reflections with even ΣH_i ($\Sigma H_i = 4$ being an exception) much stronger than can be accounted for by the americium contribution. This feature of the intensity distribution necessitates placing the potassium atom in the position ($^1/_2,{}^1/_2,{}^1/_2$).

The position deduced for the potassium atom strongly suggests the presence of an inversion center and hence equivalence between the two oxygen atoms and between the two fluorine atoms. Assuming such equivalence, the space group symmetry becomes $R\bar{3}m$ with the atomic positions: 1 Am in (0,0,0), 1 K in ($^1/_2,{}^1/_2,{}^1/_2$), 2 O in $\pm$ (u,u,u), 2 F in $\pm$ (v,v,v).

With the small scattering powers of oxygen and fluorine, it is not possible to locate these atoms with any degree of accuracy from the rather crude intensity data. Approximate values of the parameters u and v can, however, be found. In column 5 of Table I are given the intensities calculated on the basis of the americium and potassium scattering. Comparison of columns 5 and 7 shows that the observed intensities of reflections for which ΣH_i = 4, 5 and 7 are considerably weaker than can be accounted for in terms of americium and potassium atoms. The parameter values u and v are accordingly such as to give large negative contributions to the structure factor for these reflections, and this requirement gives: $u \approx 0.10$, $v \approx 0.34$.

With the deduced parameter values, each americium atom forms two short bonds with oxygen atoms giving a collinear radical $[AmO_2]^+$ (the possibility $u \approx 0.34$, $v \approx 0.10$ is rejected, since it corresponds to the unreasonable conclusion of radicals $[AmF_2]^{+3}$) and six long bonds to fluorine atoms. Each potassium atom is bonded formally to two fluorine atoms and to six oxygen atoms.

The only accurate determination of the size of an XO_2 radical is for $[UO_2]^{+2}$ in $MgUO_2O_2$, and this gave U–O = 1.93 ± 0.03 Å.[10] For the $[UO_2]^+$ group a reasonable estimate is U–O = 1.96 Å. An 0.03 Å. decrease due to the 5+ contraction in going from uranium to americium gives 1.93 Å. as an expected value for Am–O in $[AmO_2]^+$ and a parameter value $u = 0.102$.

In KF, the distance of the six K–F bonds is 2.66 Å. Since potassium has a coördination number of eight in $KAmO_2F_2$, the anticipated K–F distance is therefore 2.74 Å. requiring $v = 0.356$.

The parameter values $u = 0.102$, $v = 0.356$ will be used in preference to the direct result $u \approx 0.10$, $v \approx 0.34$. The calculated intensities, with all atoms considered, are listed in column 6 of Table I using the relationship

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

where p is the multiplicity factor, and A is the ab-

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[9] The values for the oxygen radicals are determined by the number of oxygen atoms.

[10] W. H. Zachariasen, unpublished work.

sorption factor for a cylindrical sample with μR = 3.0.

The structure found for $KAmO_2F_2$ is of the $CaUO_2O_2$ type.[11] The interatomic distances are

$$\begin{aligned} \text{Am} - 2\ \text{O} &= (1.93\ \text{Å.}) \\ \text{Am} - 6\ \text{F} &= 2.47\ \text{Å.} \\ \text{K} - 6\ \text{O} &= 2.73\ \text{Å.} \\ \text{K} - 2\ \text{F} &= (2.74\ \text{Å.}) \end{aligned}$$

the values in parentheses being assumed. The Am–F and K–O distances are not much affected by moderate variations in the parameter values u and v, and are therefore quite accurate. The great difference between the primary Am–O bond length and the secondary Am–F bond length is worthy of notice. Table II gives results for primary and secondary bond lengths of XO_2 radicals in various crystals.

In $KPuO_2CO_3$, the six secondary bonds all lie in a plane, and the bond length is for this reason longer than otherwise might be expected. This substance apart, the experimental results indicate that the secondary X–F bonds are appreciably longer than the secondary X–O bonds, and this in turn suggests that the primary bond lengths in UO_2F_2 and $KAmO_2F_2$ may be somewhat smaller than assumed.

TABLE II

Compound	Radical	Bond length, Å. Primary	Secondary
UO_2F_2[12]	$[UO_2]^{+2}$	U − 2 O = (1.91)	U − 6 F = 2.50
$KAmO_2F_2$	$[AmO_2]^{+1}$	Am − 2 O = (1.93)	Am − 6 F = 2.47
$MgUO_2O_2$[13]	$[UO_2]^{+2}$	U − 2 O = 1.93 ± 0.03	U − 4 O = 2.18
$CaUO_2O_2$	$[UO_2]^{+2}$	U − 2 O = 1.91 ± 0.10	U − 6 O = 2.29
$KPuO_2CO_3$[4]	$[PuO_2]^{+1}$	Pu − 2 O = (1.94)	Pu − 6 O = 2.55

The $KAmO_2F_2$ structure is built up of hexagonal layers $[AmO_2F_2]^-$ held together by the potassium ions. These layers are isostructural with the UO_2F_2 layers in uranyl fluoride and with the $[UO_2O_2]^{-2}$ layers in $CaUO_2O_2$. The period is 4.22 Å. for the $[AmO_2F_2]^-$ layer and 4.20 Å. for the UO_2F_2 layer as against 3.87 Å. for the $[UO_2O_2]^{-2}$ layer.

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(11) W. H. Zachariasen, *Acta Cryst.*, **1**, 281 (1948).

(12) W. H. Zachariasen, *ibid.*, **1**, 277 (1948).

(13) W. H. Zachariasen, unpublished result.

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Lattice Parameters of Some Rare Earth Compounds and a Set of Crystal Radii

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Unit cell dimensions are given for the compounds $CeCl_3$, $PrCl_3$, $SmCl_3$, $EuCl_3$ and $GdCl_3$ (hexagonal UCl_3 type), Sm_2O_3, Eu_2O_3, Gd_2O_3, Dy_2O_3, Ho_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3 and Lu_2O_3 (cubic Mn_2O_3 type), TbF_4 (monoclinic UF_4 type), and TbOF (rhombohedral LaOF type). A set of empirical crystal radii for the trivalent rare earth ions is proposed.

In the course of our studies of the crystal chemistry of rare earth compounds we have determined the lattice dimensions of several compounds of known structure type. In certain cases no lattice dimensions have been reported previously, and in others the new values are believed to be more reliable because of better purity of the rare earth compounds. These results are derived from powder diffraction patterns obtained with Cu Kα (λ 1.5418 Å.) or Cr Kα (λ 2.2909 Å.) radiation in cameras of 9 cm. diameter.

Hexagonal Trichlorides.—The trichlorides of the elements lanthanum through gadolinium were shown to be isostructural by Bommer and Hohmann.[1] Zachariasen[2] showed that they are hexagonal and worked out the atomic positions for the isostructural uranium trichloride. No lattice dimensions seem to have been reported for $SmCl_3$, $EuCl_3$ or $GdCl_3$. Our results (Cr Kα radiation) are listed in Table I, where the prior values of Zachariasen[2] are given in parentheses for comparison. For $CeCl_3$ and $PrCl_3$, which were studied in both researches, the agreement is good.

Our sample of $SmCl_3$ was prepared by Dr. H. R. Lohr, and the others by Dr. C. W. Koch by the reaction of the respective oxides with hydrogen chloride gas at 800 to 900°K.

TABLE I

LATTICE PARAMETERS OF HEXAGONAL TRICHLORIDES

	a, Å.	c, Å.	V, Å.^{3}
$LaCl_3$	(7.483 ± 0.003)[a]	(4.375 ± 0.003)[a]	212.2
$CeCl_3$	7.450 ± .004	4.315 ± .002	207.4
	(7.451 ± .004)[a]	(4.313 ± .004)[a]	
$PrCl_3$	7.422 ± .005	4.275 ± .004	203.9
	(7.42 ± .01)[a]	(4.26 ± .01)[a]	
$NdCl_3$	(7.396 ± .004)[a]	(4.239 ± .003)[a]	200.8
$SmCl_3$	7.378 ± .007	4.171 ± .004	196.6
$EuCl_3$	7.369 ± .004	4.133 ± .002	194.4
$GdCl_3$	7.363 ± .004	4.105 ± .002	192.7

[a] W. H. Zachariasen (reference 2). Changed from kX. units.

Cubic Sesquioxides.—Most of the sesquioxides of the rare earth elements as commonly prepared have the cubic Mn_2O_3 type structure[3]. The atomic positions are given for the mineral bixbyite, $(Fe,Mn)_2O_3$, by Pauling and Shappell.[4] We have calculated cell dimensions (Cu Kα radiation) for samples whose purity is greater than 99.9% according to spectrographic analysis for metallic impurities. These samples, purified by ion-exchange methods, were originally obtained from the Institute for Atomic Research, Iowa State College. The results are compared in Table II with some of the prior values found in the literature. In several

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(1) H. Bommer and E. Hohmann, *Z. anorg. allgem. Chem.*, **248**, 373 (1941).

(2) W. H. Zachariasen, *J. Chem. Phys.*, **16**, 254 (1948).

(3) *Strukturbericht*, Vol. II, p. 38.

(4) L. Pauling and M. D. Shappell, *Z. Krist.*, **75**, 128 (1930).