sorption factor for a cylindrical sample with $\mu R = 3.0$.

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

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

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[13] W. H. Zachariasen, unpublished result.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, BERKELEY]

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

BY D. H. TEMPLETON AND CAROL H. DAUBEN

RECEIVED JUNE 24, 1954

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).

cases the differences are significant. The new values, when plotted as a function of atomic number, fall somewhat better on a curve which is smooth except for a cusp at gadolinium.

For the atomic parameters given by Pauling and Shappell,[4] which we have found also to be suitable for Am_2O_3,[5] each metal atom has six oxygen neighbors at an average distance of $0.21441a$, where a is the cell dimension.

Terbium Tetrafluoride.—Dr. D. C. Feay[6] prepared TbF_4 by the reaction of TbF_3 with fluorine gas at 320°. The powder patterns, while not excellent, were identified as those of TbF_4 by the similarity with those of CeF_4 and UF_4.[7,8] The pattern was indexed (Table III) according to a monoclinic unit cell with the dimensions

$$a = 12.11 \pm 0.06 \text{ Å.}$$
$$b = 10.15 \pm 0.05$$
$$c = 7.92 \pm 0.04$$
$$\beta = 126.1 \pm 0.5°$$

The compounds ZrF_4, HfF_4,[9] ThF_4, NpF_4, PuF_4[7] and AmF_4[10] also have this structure. Zachariasen[7] determined approximate metal atom positions for UF_4. Burbank,[8] with single crystal data for UF_4, refined the structure given by Zachariasen and obtained also the fluorine positions. The space group is $C_{2h}^6 - C2/c$ with twelve molecules in the unit cell. For TbF_4 the cell volume is 786 Å.[3] and the density calculated from the X-ray data is 5.95 g. cm.$^{-3}$.

TABLE II

LATTICE DIMENSIONS OF CUBIC RARE EARTH OXIDES

Compound	Cell dimensions, Å. This research	Previous workers[d]	
Sm_2O_3	10.932 ± 0.009	10.922[a]	10.91_5[b]
Eu_2O_3	10.866 ± .005	10.862[a]	10.86_4[b]
Gd_2O_3	10.813 ± .005	10.820[a]	10.81_9[b]
Dy_2O_3	10.667 ± .006	10.65_0[b]	
Ho_2O_3	10.607 ± .005	10.60[c]	
Er_2O_3	10.547 ± .003	10.52_6[b]	
Tm_2O_3	10.488 ± .006	10.47_6[b]	
Yb_2O_3	10.439 ± .007	10.42_9[b]	
Lu_2O_3	10.391 ± .005	10.39_6[b]	

[a] A. Iandelli, *Gazz. chim. ital.*, **77**, 312 (1947). [b] H. Bommer, *Z. anorg. allgem. Chem.*, **241**, 273 (1939). [c] W. H. Zachariasen, *Norske Vid. Akad. Oslo*, I, Mat. Nat. Kl. 4, 1 (1928). [d] The values cited from *a*, *b* and *c* have been changed from kX. units.

TABLE III

POWDER DIFFRACTION DATA FOR TbF_4

(Cr Kα, λ = 2.2909 Å.)

hkl	$\sin^2\theta$ Calcd.	$\sin^2\theta$ Obsd.	*I*, obsd.[a]
110	0.0264	0.0260	w
$11\bar{1}$	.0338	.0331	w
021	.0831	.0826	s
111	.0832		
$20\bar{2}$	.0841		
$31\bar{1}$	.0941	.0936	m
$11\bar{2}$	.1051	.1052	vs
220	.1059		
$31\bar{2}$	.1160	.1160	m
002	.1282	.1287	w
130	.1284		
$22\bar{2}$	.1352	.1347	m
$13\bar{1}$	.1358		
310	.1362		
422	.2009	.2015	w
$31\bar{3}$	.2021		
$42\bar{1}$	.2037		
040	.2038		
112	.2041		
330	.2382	.2382	vw
$33\bar{3}$	.3041	.3034	vw
$60\bar{2}$	.3253	.3257	w
042	.3320	.3335	w
150	.3322		
222	.3330		
$53\bar{2}$	.3386	.3404	m
023	.3395		
$15\bar{1}$	.3396		
241	.3403		

[a] v = very, s = strong, m = medium, w = weak.

Terbium Oxyfluoride.—Feay[6] also prepared TbOF by pyrohydrolysis of TbF_4 at 400° in a muffle furnace for about ten hours. The pattern (Cu Kα) was pseudo-cubic with considerable broadening of some of the lines. With chromium Kα radiation the doubling of several of these lines was resolved. Comparison of the intensities and line structure with the data of Zachariasen[11] for the tetragonal and rhombohedral forms of YOF and LaOF showed clearly that the TbOF was rhombohedral. The diffraction data (Table IV) correspond to a rhombohedral cell with

$$a = 6.751 \pm 0.005 \text{ Å.}$$
$$\alpha = 33.09 \pm 0.03°$$

Zachariasen[11] found the space group $D_{3d}^5 - R\bar{3}m$ with two molecules in the unit cell and reported atomic positions for LaOF which were satisfactory for YOF also. The parameters cannot be very different for TbOF as the intensities agree well with those observed by Zachariasen for LaOF. With these parameters, each terbium atom has four oxygen neighbors at 2.45 Å. and four fluorine neighbors at 2.30 Å. The structure is a superlattice based on a slightly distorted CaF_2 type structure. For the undistorted structure α is 33.56°.[12] For TbOF the unit cell volume is 244.8 Å.[3] and the X-ray density 7.89 g. cm.$^{-3}$.

Empirical Crystal Radii.—One of the chief uses of crystal radii is the correlation of various thermodynamic properties. In the rare earth series this is not satisfactory if the radii are expressed to two decimal places as is customary, since the differences between adjacent elements are of the same order of magnitude as the possible rounding-off errors.[13] For this reason, we list in Table V a set of empirical crystal radii for the trivalent rare earth ions, given

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(5) D. H. Templeton and C. H. Dauben, THIS JOURNAL, **75**, 4560 (1953).

(6) B. B. Cunningham, D. C. Feay and M. A. Rollier, *ibid.*, **76**, 3361 (1954).

(7) W. H. Zachariasen, *Acta Cryst.*, **2**, 388 (1949).

(8) R. D. Burbank, Atomic Energy Commission Declassified Document, AECD-3216, August, 1951.

(9) G. E. R. Schulze, *Z. Krist.*, **89**, 477 (1934).

(10) L. B. Asprey, THIS JOURNAL, **76**, 2019 (1954).

(11) W. H. Zachariasen, *Acta Cryst.*, **4**, 231 (1951).

(12) The value 33.22° given in reference 11 is incorrect.

(13) A recent example of such difficulties is given by Wheelwright, Spedding and Schwarzenbach, THIS JOURNAL, **75**, 4196 (1953).

TABLE IV

POWDER DIFFRACTION DATA FOR TbOF

(Cr Kα, λ = 2.2909 Å.)

hkl[a] hex.	*hkl*, rhomb.	$\sin^2\theta$ Calcd.	$\sin^2\theta$ Obsd.	*I*, obsd.
006	222	0.1291	0.1284	w
102	110	.1327	.1325	ms
104	211	.1758	.1759	m
009	333	.2905	.2919	vw
107	322	.2941		
108	332	.3480	.3482	m
110	$10\bar{1}$	.3551	.3550	m+
201	$11\bar{1}$	.4771	.4768	w
1, 0, 10	433	.4771		
116	321	.4842	.4857[b]	m
202	200	.4878		
204	220	.5309	.5310	w
1, 0, 11	443	.5524	.5519	vw
119	432	.6456	.6478	w
207	331	.6493		
208	422	.7031	.7037	mw
1, 0, 13	544	.7246	.7232	vw
0, 0, 15	555	.8071	.8095	trace
1, 0, 14	554	.8215	.8215	w
2, 0, 10	442	.8322	.8316	w
211	$20\bar{1}$	.8323		
212	$21\bar{1}$	.8430	.8430	m+
1, 1, 12	543	.8716	.8713	w
214	310	.8861	.8857	m

[a] For an hexagonal cell with $a = 3.844$, $c = 19.13$, $Z = 6$. [b] Diffuse.

to three decimal places. It should be remembered that the second decimal is in doubt on an absolute scale, but the third decimal is of significance in the *differences* of adjacent radii. For most correlative purposes, the absolute scale is of no consequence.

These radii are based primarily on the cubic oxides, with the radius of oxygen taken as 1.380 Å. in this structure (coördination six). The cell dimensions of the tetragonal oxychlorides,[14] the second most extensive isostructural set available, were used in an empirical way to help fix the values for the elements near lanthanum. The less extensive data on the monoclinic[15] and hexagonal chlorides and orthorhombic fluorides[16] were used to test the curvature of the plot of radius against atomic number. About as many deviations occurred in one direction as in the other.

TABLE V

CRYSTAL RADII OF TRIVALENT RARE EARTH IONS

Ion	Radius, Å.	Ion	Radius, Å.
La^{+++}	1.061	Tb^{+++}	0.923
Ce^{+++}	1.034	Dy^{+++}	.908
Pr^{+++}	1.013	Ho^{+++}	.894
Nd^{+++}	0.995	Er^{+++}	.881
Pm^{+++}	.979	Tm^{+++}	.869
Sm^{+++}	.964	Yb^{+++}	.858
Eu^{+++}	.950	Lu^{+++}	.848
Gd^{+++}	.938		

We wish to thank Mrs. Helena W. Ruben who took the diffraction photographs and performed some of the calculations, and Professor B. B. Cunningham and his students who supplied us with the rare earth trichlorides and the terbium compounds. The completion of this study was aided by a John Simon Guggenheim Memorial Fellowship (to D.H.T.) and by the kind hospitality of Professor G. Hägg and the Institute of Chemistry, University of Uppsala, Uppsala, Sweden. This research was supported by the Atomic Energy Commission.

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(14) D. H. Templeton and C. H. Dauben, THIS JOURNAL, 75, 6069 (1953).

(15) D. H. Templeton and G. F. Carter, *J. Phys. Chem.*, 58, Nov. (1954).

(16) A. Zalkin and D. H. Templeton, THIS JOURNAL, 75, 2453 (1953).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

Praseodymium Oxides. II. X-Ray and Differential Thermal Analyses[1]

BY E. DANIEL GUTH,[2] J. R. HOLDEN, N. C. BAENZIGER AND LEROY EYRING

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This is a study of oxides of praseodymium in the composition range Pr_2O_3 to Pr_6O_{11}. X-Ray powder diagrams of quenched samples were taken in order to investigate the structures of oxides of several compositions. High temperature X-ray powder diagrams were taken for a check on the quenching procedure. Differential thermal analyses were made to further illustrate the stepwise nature of oxidation and reduction in this system. The results indicate that under equilibrium conditions oxides with hexagonal, body-centered cubic, rhombohedral or face-centered cubic lattices are stable at various compositions. As Pr_6O_{11} is reduced to Pr_2O_3 it undergoes changes in lattice from face-centered cubic to rhombohedral to body centered cubic to hexagonal. Each of these lattices is found to be stable over a range of compositions. The rhombohedral lattice has not previously been reported.

Introduction

Dissociation pressure measurements on praseodymium oxides[3] indicate that in addition to the well-known oxides, Pr_2O_3 and Pr_6O_{11}, other oxides intermediate to them exhibit stability under equilibrium conditions at particular pressures up to one atmosphere of oxygen, and temperatures up to 1050°. Many previous workers have reported Pr_2O_3 and Pr_6O_{11}, but the nature of the region between these compositions has not been clearly understood. Through the techniques of X-ray diffraction and differential thermal analysis a study of this system has been carried out to further elucidate it.

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(1) Part of the data reported here was taken from a dissertation submitted by E. Daniel Guth to the Graduate College of the State University of Iowa.

(2) Research Division, Phillips Petroleum Co., Bartlesville, Oklahoma.

(3) R. Ferguson, E. Daniel Guth and L. Eyring, THIS JOURNAL, 76, 3890 (1954).