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Contract No. W-7405-eng-48

# LATTICE PARAMETERS OF SOME RARE EARTH COMPOUNDS AND A SET OF CRYSTAL RADII

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June 1, 1954

Berkeley, California

(Contribution from the Department of Chemistry and Radiation Laboratory, University of California, Berkeley 4, California)

# LATTICE PARAMETERS OF SOME RARE EARTH COMPOUNDS AND A SET OF CRYSTAL RADII

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## ABSTRACT

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 CuKα (λ1.5418 Å) or CrKα (λ2.2909 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]

1. H. Bommer and E. Hohmann, Z. anorg. allgem. Chem., 248, 373 (1941).
2. W. H. Zachariasen, J. Chem. Phys., 16, 254 (1948).

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 (CrKα 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 | c | V |
|---|---|---|---|
| $LaCl_3$ | (7.483 ± 0.003 Å)[a] | (4.375 ± 0.003 Å)[a] | 212.2 Å$^3$ |
| $CeCl_3$ | 7.450 ± 0.004<br>(7.451 ± 0.004)[a] | 4.315 ± 0.002<br>(4.313 ± 0.004)[a] | 207.4 |
| $PrCl_3$ | 7.422 ± 0.005<br>(7.42 ± 0.01)[a] | 4.275 ± 0.004<br>4.26 ± 0.01)[a] | 203.9 |
| $NdCl_3$ | (7.396 ± 0.004)[a] | (4.239 ± 0.003)[a] | 200.8 |
| $SmCl_3$ | 7.378 ± 0.007 | 4.171 ± 0.004 | 196.6 |
| $EuCl_3$ | 7.369 ± 0.004 | 4.133 ± 0.002 | 194.4 |
| $GdCl_3$ | 7.363 ± 0.004 | 4.105 ± 0.002 | 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

3. Strukturbericht II, p. 38.

atomic positions are given for the mineral bixbyite, $(Fe, Mn)_2O_3$, by Pauling and Shappell.[4] We have calculated cell dimensions

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

(CuKα 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 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

5. D. H. Templeton and C. H. Dauben, J. Am. Chem. Soc., 75, 4560 (1953).

atom has six oxygen neighbors at an average distance of 0.21441 a, where a is the cell dimension.

## Terbium Tetrafluoride

Dr. D. C. Feay[6] prepared $TbF_4$ by the reaction of $TbF_3$ with

6. B. B. Cunningham, D. C. Feay, and M. A. Rollier, J. Am. Chem. Soc., in press.

fluorine gas at 320° C. 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

7. W. H. Zachariasen, Acta Cryst., 2, 388 (1949).
8. R. D. Burbank, Atomic Energy Commission Declassified Document, AECD-3216, August, 1951.

monoclinic unit cell with the following dimensions:

$$\underline{a} = 12.11 \pm 0.06 \text{ Å}$$

$$\underline{b} = 10.15 \pm 0.05$$

$$\underline{c} = 7.92 \pm 0.04$$

$$\beta = 126.1 \pm 0.5^{\circ}$$

Table II

Lattice Dimensions of Cubic Rare Earth Oxides

| Compound | Cell dimensions | | |
|---|---|---|---|
| | This research | Previous workers[d] | |
| $Sm_2O_3$ | 10.932 ± 0.009 Å | 10.922[a] | $10.91_5$[b] Å |
| $Eu_2O_3$ | 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.

The compounds $ZrF_4$, $HfF_4$,[9] $ThF_4$, $NpF_4$, $PuF_4$,[7] and $AmF_4$[10]

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

10. L. B. Asprey, J. Am. Chem. Soc., 76, 2019 (1954).

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 III

Powder Diffraction Data for $TbF_4$
(CrK$\alpha$, $\lambda$ = 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 | | |
| 111 | .0832 | .0826 | s |
| 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 | | |
| 13$\bar{1}$ | .1358 | .1347 | m |
| 310 | .1362 | | |
| 422 | .2009 | | |
| 31$\bar{3}$ | .2021 | | |
| 42$\bar{1}$ | .2037 | .2015 | w |
| 040 | .2038 | | |
| 112 | .2041 | | |
| 330 | .2382 | .2382 | vw |
| 33$\bar{3}$ | .3041 | .3034 | vw |
| 60$\bar{2}$ | .3253 | .3257 | w |

Table III (cont'd)

| hkℓ | $\sin^2\theta$ calcd. | $\sin^2\theta$ obsd. | I obsd.[a] |
|---|---|---|---|
| 042 | 0.3320 | | |
| 150 | .3322 | 0.3335 | w |
| 222 | .3330 | | |
| 53$\bar{2}$ | .3386 | | |
| 023 | .3395 | .3404 | m |
| 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° C in a muffle furnace for about ten hours. The pattern (CuKα) 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

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

YOF and LaOF showed clearly that the TbOF was rhombohedral. The diffraction data (Table IV) correspond to a rhombohedral cell with

$$a = 6.751 \pm 0.005 \text{ Å}$$

$$\alpha = 33.09 \pm 0.03^\circ$$

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 $\underline{a}$ is 33.56°.[12]

12. The value 33.22° given in Reference 11 is incorrect.

For TbOF the unit cell volume is 244.8 $Å^3$ and the X-ray density 7.89 g. cm.$^{-3}$.

Table IV

Powder Diffraction Data for TbOF
(CrK$\underline{\alpha}$, $\underline{\lambda}$ = 2.2909 Å)

| $\underline{hk\ell}$ [a] hex. | $\underline{hk\ell}$ 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* | m |
| 202 | 200 | .4878 | | |

Table IV (cont'd)

| hkℓ[a] hex. | hkℓ rhomb. | $\sin^2\theta$ calcd. | $\sin^2\theta$ obsd. | I obsd. |
|---|---|---|---|---|
| 204 | 220 | 0.5309 | 0.5310 | 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.

*diffuse

## 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]

13. A recent example of such difficulties is given by Wheelwright, Spedding and Schwarzenbach, J. Am. Chem. Soc., 75, 4196 (1953).

For this reason, we list in Table V a set of empirical crystal radii for the trivalent rare earth ions, given 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 (coordination six). The cell dimensions of the tetragonal oxychlorides,[14] the second

14. D. H. Templeton and C. H. Dauben, J. Am. Chem. Soc., 75, 6069 (1953).

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

15. D. H. Templeton and G. F. Carter, J. Phys. Chem., in press.

and orthorhombic fluorides[16] were used to test the curvature of the

16. A. Zalkin and D. H. Templeton, J. Am. Chem. Soc., 75, 2453 (1953).

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 | Ion | Radius |
|---|---|---|---|
| $La^{+++}$ | 1.061 Å | $Tb^{+++}$ | 0.923 |
| $Ce^{+++}$ | 1.034 | $Dy^{+++}$ | 0.908 |
| $Pr^{+++}$ | 1.013 | $Ho^{+++}$ | 0.894 |
| $Nd^{+++}$ | 0.995 | $Er^{+++}$ | 0.881 |
| $Pm^{+++}$ | 0.979 | $Tm^{+++}$ | 0.869 |
| $Sm^{+++}$ | 0.964 | $Yb^{+++}$ | 0.858 |
| $Eu^{+++}$ | 0.950 | $Lu^{+++}$ | 0.848 |
| $Gd^{+++}$ | 0.938 | | |

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.