UCRL-17710
c.2

University of California

Ernest O. Lawrence Radiation Laboratory

CRYSTAL STRUCTURES AND LATTICE PARAMETERS
OF THE COMPOUNDS OF BERKELIUM.
II. BERKELIUM TRICHLORIDE

J. R. Peterson and B. B. Cunningham

August 2, 1967

TWO-WEEK LOAN COPY

This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545

UCRL-17710
c.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Submitted to Journal of Inorganic
and Nuclear Chemistry

UCRL-17710
Preprint

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

CRYSTAL STRUCTURES AND LATTICE PARAMETERS OF THE COMPOUNDS OF BERKELIUM. II. BERKELIUM TRICHLORIDE

J. R. Peterson and B. B. Cunningham

August 2, 1967

CRYSTAL STRUCTURES AND LATTICE PARAMETERS OF THE COMPOUNDS OF BERKELIUM. II. BERKELIUM TRICHLORIDE

J. R. Peterson and B. B. Cunningham

Department of Chemistry and Lawrence Radiation Laboratory
University of California
Berkeley, California

August 2, 1967

ABSTRACT

$BkCl_3$ has been prepared and found to exhibit the UCl_3-type hexagonal structure. Powder data from three samples give average lattice parameters $a_o = 7.382 \pm .002$ A and $c_o = 4.127 \pm .003$ A, where the error limits are the 95% confidence interval calculated using the standard statistical method for the average of three independent determinations.

CRYSTAL STRUCTURES AND LATTICE PARAMETERS OF THE COMPOUNDS OF BERKELIUM. II. BERKELIUM TRICHLORIDE*

J. R. Peterson and B. B. Cunningham

Department of Chemistry and Lawrence Radiation Laboratory
University of California
Berkeley, California

August 2, 1967

INTRODUCTION

As part of a continuing program to investigate the crystallographic properties of berkelium, we report here our results for the UCl_3-type hexagonal berkelium trichloride.

EXPERIMENTAL

The source of berkelium was the same as reported previously.(1) The lime-green trichloride samples were prepared by treatment of the oxides, contained in quartz x-ray capillaries, with anhydrous HCl gas at ~520° C for three 10-12 min periods interrupted by cooling, evacuation and admission of fresh HCl. The HCl gas was allowed to flow through the capillary system at atmospheric pressure. The techniques employed in this hydrochlorination have been published previously.(2,3)

All $BkCl_3$ samples prepared exhibited the UCl_3-type hexagonal structure.

Exposure times were about 10 hours, using the same diffraction equipment and operating conditons as reported for the oxide work.(1)

---

*The experimental work reported here is taken from a thesis to be submitted by J. R. Peterson to the Graduate Division of the University of California in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

RESULTS AND DISCUSSION

Powder data were treated as reported in the first paper of this series.[1] The theoretical intensity calculations were carried out assuming the atomic coordinates of UCl_3[4] for those of $BkCl_3$.

Table 1 lists the observed lattice parameters for the individual trichloride preparations along with their Cf^{249} content. Films 2587A and 2598A showed pure trichloride phases, whereas Film 2600A showed mixed phases of $BkCl_3$ and BkOCl, predominantly the former. Film 2652A was a second exposure of sample number JRP-XVI (Film 2598A) after an 85-day time lapse. This was to see if the lattice parameters would shift noticeably toward those of $CfCl_3$ as the Cf^{249} content in the $BkCl_3$ increased. Comparison with the UCl_3-type hexagonal $CfCl_3$ lattice parameters,[3,5] $a_o = 7.393 \pm .040$ A and $c_o = 4.090 \pm .060$ A, clearly shows the expected expansion in the a_o parameter and shrinkage in the c_o parameter.

In accordance with Vegard's Law (assuming ideal homogeneous solid solutions), the observed lattice parameters were corrected for the known Cf and Ce content (0.27 atom %), then averaged to obtain "best estimates" for "pure" $BkCl_3$: $a_o = 7.382 \pm .002$ A, $c_o = 4.127 \pm .003$ A. The error limits placed on these average lattice parameter values were computed using the 95% confidence level = $(4.30/\sqrt{N})\sqrt{\frac{\Sigma d_i^2}{N-1}}$, where d_i is the deviation of the individual lattice parameters from the average value, N is the number of observations, and the factor 4.30 is the 95% confidence Student t value for three observations.

Table 2 gives the line list and indexing for one of the $BkCl_3$ samples, the calculated 2θ values, and the observed and calculated line intensities.

Plots of the a_o and c_o lattice parameters for the UCl_3-type hexagonal actinide trichlorides are given in Figs.1(a) and 1(b), respectively. These plots show that, in the case of the actinide trichlorides, the "actinide contraction" is clearly anisotropic.

Usually such a series of isomorphic compounds lends itself for calculation of the corresponding ionic radii; however, because of the anisotropies in this trichloride series, the concept of ionic radius should be regarded with considerable caution. Radii calculations are based on averaged interatomic distances; and the radius concept begins to lose meaning when the distances averaged are considerably different. Table 3 lists the M-Cl bond distances in the UCl_3-type actinide trichlorides along with calculated six-fold coordinated trivalent ionic radii. Calculations similar to those presented in Table 3 show that the lanthanide trichlorides also exhibit an anisotropic "lanthanide contraction." Comparison of the similarly-calculated trivalent ionic radii shows almost identical values for the following lanthanide-actinide pairs: Gd-Cf, Eu-Bk, Sm-Cm, Pm-Am, Nd-Pu, Pr-Np and Ce-U.

Because of the extreme anion crowding in this UCl_3-type trichloride structure and by analogy with the lanthanide trichlorides, it is very probable that there will be a crystal structure change noted in the actinide trichlorides heavier than $CfCl_3$. In the corresponding lanthanide trichloride series, the crystal structure changes from the UCl_3-type hexagonal (Ce-Gd)[8] to the $PuBr_3$-type orthorhombic (Tb)[9] to the YCl_3-type monoclinic (Dy-Lu).[10] The realization of this prediction will have to wait until $EsCl_3$ is prepared and its crystal structure is determined.

ACKNOWLEDGMENTS

The authors thank Miss Judy Copeland for her film reading help and the Health Chemistry Group for their careful monitoring assistance.

This work was performed under the auspices of the U. S. Atomic Energy Commission.

REFERENCES

(1) J. R. Peterson and B. B. Cunningham, University of California Lawrence Radiation Laboratory Report, UCRL-17576, May 1967, submitted to Inorg. Nucl. Chem. Letters.

(2) B. B. Cunningham, Microchemical Journal Symposium (1961).

(3) J. L. Green, (Ph.D. Thesis), University of California Lawrence Radiation Laboratory Report, UCRL-16516, November 1965.

(4) W. H. Zachariasen, The Transuranium Elements, Part II, National Nuclear Energy Series, Vol. 14B, paper 20.6, Mc-Graw Hill Book Company, Inc., New York, 1949.

(5) J. L. Green and B. B. Cunningham, University of California Lawrence Radiation Laboratory Report, UCRL-17539, May 1967, submitted to Inorg. Nucl. Chem. Letters.

(6) D. K. Smith, University of California Lawrence Radiation Laboratory Report, UCRL-7196, 1963.

(7) W. H. Zachariasen, The Actinide Elements, Chapter 18, Crystal Chemistry of the 5f Elements, National Nuclear Energy Series, Vol. 14A, Mc-Graw Hill Book Company, Inc., New York, 1954.

(8) W. H. Zachariasen, Acta. Cryst. 1, 265 (1948).

(9) J. D. Forrester, Allan Zalkin, David H. Templeton, and J. C. Wallman, Inorg. Chem. 3, 185 (1964).

(10) D. H. Templeton and G. F. Carter, J. Phys. Chem. 58, 940 (1954).

TABLE 1. BERKELIUM TRICHLORIDE LATTICE PARAMETERS (UCl_3-TYPE HEXAGONAL)

Sample Number	Film Number	Cf^{249}[a] Content (atom %)	Observed Lattice Parameters[b] (A) $a_o \pm 2\sigma$	$c_o \pm 2\sigma$
JRP-XIV	2587A	3.04	7.382±.001	4.127±.001
JRP-XVI	2598A	3.68	7.384±.001	4.127±.001
JRP-XVII	2600A	3.90	7.383±.001	4.125±.001
JRP-XVI	2652A	20.17	7.387±.001	4.122±.001

[a]Calculated assuming Bk^{249} half-life is 314 days.

[b]Lattice parameters are the least squares value. The 2σ error limits represent the 95% confidence range reflecting only the internal consistency of the data for the individual preparation.

TABLE 2. LINE LIST AND INDEXING FOR $BkCl_3$ (JRP-XIV, FILM 2587A)

hkl	Observed[a] 2θ (deg)	Calculated[b] 2θ (deg)	Observed[a] Line Intensity	Calculated[c] Line Intensity
110	24.09	24.11	9.0	6.8
101	25.68	25.69	9.5	10.0
200	27.93	27.91	5.0	2.3
111	32.58	32.54	3.3	1.1
201	35.48	35.52	9.7	9.2
210	37.23	37.21	4.5	1.6
300	42.37	42.42	7.0	3.6
211	43.32	43.39	9.0	7.7
002	43.92	43.87	2.7	1.5
102	46.32	46.22	3.5	1.0
220	49.37	49.38	3.3	1.4
112	50.62	50.68	5.5	2.1
310	51.52	51.54	2.5	0.8
202	52.82	52.80	2.8	0.8
131	56.53	56.49	5.5	2.3
400	57.72	57.68	1.5	0.4
212	58.87	58.85	3.8	0.9
401	62.27	62.30	1.3	0.7
302	62.72	62.67	5.5	2.2
230	63.42	63.42	0.7	0.5
410	67.07	67.09	4.0	1.3
231	67.87	67.81	6.0 broad	2.8
222		68.17		1.1

(Continued)

TABLE 2. (Continued)

hkl	Observed[a] 2θ (deg)	Calculated[b] 2θ (deg)	Observed[a] Line Intensity	Calculated[c] Line Intensity
103	69.97	69.94	4.3	0.7
312		69.95		0.7
203	75.21	75.18	4.5	1.0
402		75.19		0.4
501	78.21	78.28	2.0	1.0
213	80.31	80.30	4.8	1.4
232		80.31		0.5
421	83.34	83.34	5.0	1.1
412	83.64	83.67	5.5	1.5
511	88.36	88.36	4.5	1.2
313	90.30	90.34	4.0	0.7
502		90.35		0.3
332	93.71	93.69	1.0	0.6
403	95.46	95.35	1.0	0.3
242		95.36		0.1
601	96.76	96.71	1.3	0.04
004		96.68		0.2
431_{α_1}	98.26	98.28	2.5 broad	0.8
104_{α_1}		98.25		0.2
512_{α_1}	100.26	100.29	4.8	0.1
323_{α_1}		100.28		0.8
512_{α_2}	100.66	100.64	2.5	0.06
323_{α_2}		100.63		0.4

(Continued)

TABLE 2. (Continued)

hkl	Observed[a] 2θ (deg)	Calculated[b] 2θ (deg)	Observed[a] Line Intensity	Calculated[c] Line Intensity
114_{α_1}	101.91	101.63	1.8 broad	0.3
214_{α_1}	108.56	108.52	3.5	0.2
161_{α_1}		108.55		0.6
602_{α_1}	109.06	108.90	3.5	0.3
503_{α_1}	110.80	110.66	3.5	0.4
432_{α_1}		110.67		0.3
503_{α_2}	111.10	111.07	2.0	0.2
432_{α_2}		111.08		0.2
304_{α_1}	112.10	112.07	3.5	0.5
304_{α_2}	112.60	112.49	2.0	0.3
252_{α_1}	114.25	114.27	3.5	0.9
423_{α_1}	116.05	116.09	3.5	0.6
423_{α_2}	116.55	116.55	1.8	0.3
224_{α_1}	117.60	117.57	1.8	0.4
224_{α_2}	118.20	118.04	1.0	0.2
701_{α_1}	119.40	119.50	3.5	0.3
531_{α_1}		119.50		0.7
314_{α_1}		119.47		0.2
513_{α_1}	121.80	121.80	4.0	0.8
612_{α_1}		121.81		0.2
513_{α_2}	122.40	122.31	2.0	0.4
612_{α_2}		122.32		0.1
404_{α_1}	125.39	125.38	3.5 broad	0.2
621_{α_1}		125.41		0.7

(Continued)

TABLE 2. (Continued)

hkl	Observed[a] 2θ (deg)	Calculated[b] 2θ (deg)	Observed[a] Line Intensity	Calculated[c] Line Intensity
710_{α_1}	130.90	130.92	1.5	0.6
324_{α_1}	131.80	131.77	1.5	0.3
442_{α_1}	132.30	132.24	2.0	0.6
433_{α_1}	134.50	134.52	3.5	0.7
702_{α_1}		134.53		0.2
532_{α_1}		134.53		0.4
433_{α_2}	135.20	135.20	2.0	0.4
702_{α_2}		135.22		0.09
532_{α_2}		135.22		0.2
414_{α_1}	136.30	136.40	4.3	1.1
414_{α_2}	137.15	137.12	2.0	0.6
450_{α_1}	140.39	140.46	1.3	0.05
105_{α_1}		140.39		0.4
262_{α_1}	142.04	142.04	1.3	0.4
541_{α_1}	147.29	147.22	3.0	1.1
504_{α_1}		147.17		0.3
800_{α_1}	149.09	149.12	2.5	0.1
205_{α_1}		149.03		0.8
800_{α_2}	149.94	150.17	1.3	0.05
205_{α_2}		150.08		0.4
163_{α_1}	151.09	151.09	4.0	1.2
163_{α_2}	152.19	152.21	1.8	0.6
334_{α_1}	153.99	153.95	2.5 broad	0.8

(Continued)

TABLE 2. (Continued)

hkl	Observed[a] 2θ (deg)	Calculated[b] 2θ (deg)	Observed[a] Line Intensity	Calculated[c] Line Intensity
334_{α_2}	154.99	155.21	1.5 broad	0.4
712_{α_1}	158.98	159.01	4.0 broad	2.9
712_{α_2}	160.73	160.60	4.0 broad	1.6
215_{α_1}		160.83		2.1

[a]Two independent observer's averaged readings (2θ readings are ±0.10°) and averaged intensities on a scale from 10 to 0.

[b]Based on the hexagonal lattice parameters a_o = 7.3817 A, c_o = 4.1274 A and $\lambda(\bar{\alpha})$ = 1.54178 A, $\lambda(\alpha_1)$ = 1.54051 A, and $\lambda(\alpha_2)$ = 1.54433 A.

[c]Calculated using the POWD intensity program[(6)] and scaled such that the most intense line had I = 10.0.

TABLE 3. ACTINIDE-CHLORIDE BOND DISTANCES AND ACTINIDE TRIVALENT IONIC RADII (DERIVED FROM UCl_3-TYPE HEXAGONAL ACTINIDE TRICHLORIDE CRYSTAL DATA)

Actinide Trichloride	Lattice Parameters (A)		M-Cl Bond Distances (A)		Ionic Radius[a] (A) (CN = 6)
	a_o	c_o	apical	equitorial	
Ac	7.64	4.56	3.092	3.036	1.153
U	7.443	4.321	2.968	2.958	1.045
Np	7.420	4.282	2.949	2.948	1.029
Pu	7.395	4.246	2.931	2.939	1.014
Am	7.384	4.225	2.922	2.934	1.006
Cm	7.380	4.185	2.907	2.933	0.996
Bk	7.382	4.127	2.886	2.933	0.982
Cf	7.393	4.090	2.875	2.938	0.976

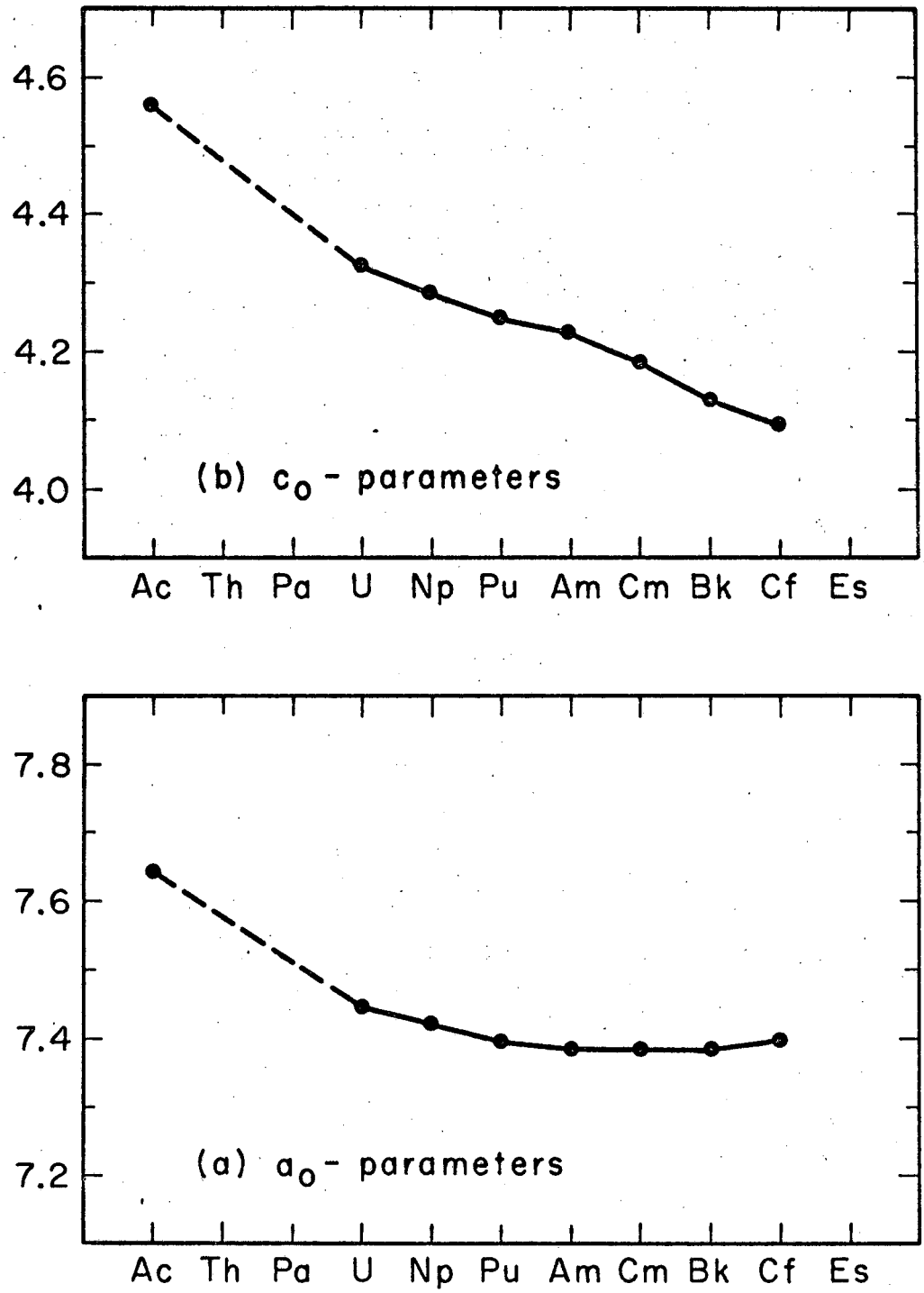
[a]Calculated according to the following formula:

$$\text{Ionic Radius} = [3(\text{M-Cl equitorial bond distance}) + 6(\text{M-Cl apical bond distance})]/9 - 1.81 - 0.11$$

where the chloride ionic radius is taken to be 1.81 A[7] and the 9-fold to 6-fold coordination correction number is taken to be 0.11 A.[7]

FIGURE CAPTIONS

Figs. 1(a) and 1(b). Lattice parameters for the UCl_3-type hexagonal actinide trichlorides.



XBL678-3625

Figs. 1(a) and 1(b)

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.