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

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Abstract – BkCl<sub>3</sub> has been prepared and found to exhibit the UCl<sub>3</sub>-type hexagonal structure. Powder data from three samples give average lattice parameters  $a_0 = 7.382 \pm 0.002 A$  and  $c_0 = 4.127 \pm 0.003 A$ , where the error limits are the 95 per cent confidence interval calculated using the standard statistical method for the average of three independent determinations.

### 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  $\sim$ 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<sub>3</sub> samples prepared exhibited the UCl<sub>3</sub>-type hexagonal structure.

Exposure times were about 10 hr, using the same diffraction equipment and operating conditions as reported for the oxide work [1].

## **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 co-ordinates 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<sup>249</sup> content. Films 2587A and 2598A showed pure trichloride phases, whereas Film 2600A showed mixed phases of BkCl<sub>3</sub> 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

\*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.

- 1. J. R. Peterson and B. B. Cunningham, Inorg. nucl. chem. Letters 3, 327 (1967).
- 2. B. B. Cunningham, Microchemical Journal, Symposium, pp. 69-93. Interscience, New York (1961).
- 3. J. L. Green, (Ph.D. Thesis), University of California Lawrence Radiation Laboratory Rep. No. UCRL-16516 (1965).
- 4. W. H. Zachariasen, The Transuranium Elements, Part II, Vol. 14B, paper 20.6. McGraw-Hill, New York (1949).

Sample	Film	Cf <sup>249</sup> *	Observed lattice parameters †(A)		
number	number	(atom per cent)	$a_0 \pm 2\sigma$	$c_0 \pm 2\sigma$	
JRP-XIV	2587A	3.04	$7.382 \pm 0.001$	$4.127 \pm 0.001$	
JRP-XVI	2598A	3.68	$7.384 \pm 0.001$	$4.127 \pm 0.001$	
JRP-XVII	2600A	3.90	$7.383 \pm 0.001$	$4.125 \pm 0.001$	
JRP-XVI	2652A	20.17	$7.387 \pm 0.001$	$4{\cdot}122\pm0{\cdot}001$	

Table 1. Berkelium trichloride lattice parameters (UCl<sub>3</sub>-type hexagonal)

\*Calculated assuming Bk<sup>249</sup> half life is 314 days.

†Lattice parameters are the least squares value. The  $2\sigma$  error limits represent the 95 per cent confidence range reflecting only the internal consistency of the data for the individual preparation.

see if the lattice parameters would shift noticeably toward those of CfCl<sub>3</sub> as the Cf<sup>249</sup> content in the BkCl<sub>3</sub> increased. Comparison with the UCl<sub>3</sub>-type hexagonal CfCl<sub>3</sub> lattice parameters [3, 5],  $a_0 = 7.393 \pm 0.040A$  and  $c_0 = 4.090 \pm 0.060A$ , clearly shows the expected expansion in the  $a_0$  parameter and shrinkage in the  $c_0$  parameter.

In accordance with Vegard's Law (assuming ideal homogeneous solid solutions), the observed lattice parameters were corrected for the known Cf and Ce contents (0.27 atom per cent), then averaged to obtain "best estimates" for "pure" BkCl<sub>3</sub>:  $a_0 = 7.382 \pm 0.002 A$ ,  $c_0 = 4.127 \pm 0.003 A$ . The error limits placed on these average lattice parameter values were computed using the 95 per cent confidence level =  $(4.30/\sqrt{N})\sqrt{[\Sigma d_i^2/(N-1)]}$ , 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 per cent confidence Student t value for three observations.

Table 2 gives the line list and indexing for one of the BkCl<sub>3</sub> samples, the calculated  $2\theta$  values, and the observed and calculated line intensities.

Plots of the  $a_0$  and  $c_0$  lattice parameters of the UCl<sub>3</sub>-type hexagonal actinide trichlorides are given in Fig. 1(a) and (b), respectively. These plots show that, in the case of the actinide trichlorides, the "actinide contraction" is clearly anisotropic.

hki	Observed* 2θ (deg)	Calculated† 2θ (deg)	Observed* line intensity	Calculated‡ 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	

Table 2. Line list and indexing for BkCl<sub>3</sub> (JRP-XIV, Film 2587A)

5. J. L. Green and B. B. Cunningham, Inorg. nucl. chem. Lett. 3, 343 (1967).

	Observed*	Calculated <sup>†</sup>	Observed*	Calculated	
hkl	2θ (deg)	2θ (deg)	line intensity	line intensity	
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	
31	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	
\$01	62.27	62.30	1.3	0.7	
302	62.72	62.67	5.4	2.2	
230	63-42	63.42	0.7	0.5	
410	67.07	67.09	4.0	1.3	
231)		67.81		(2.8	
222	67.87	68.17	6∙0 broad	1.1	
103)	<0.0 <b>7</b>	69.94		(0.7	
312	69.97	69-95	4.3	<b>(0</b> ∙7	
203)		75-18		(1.0	
402	75-21	75.19	4.5	<b>10.4</b>	
501	<b>78</b> ·21	78.28	2.0	1.0	
213)	<b>DO 31</b>	80.30	4.0	(1.4	
232	80-31	80.31	4.8	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)	90.20	90.34	4.0	<b>(0</b> ∙7	
502)	30.30	90.35	4.0	<b>(0-3</b>	
332	93·71	93.69	1.0	0.6	
403]	95.46	95.35	1.0	<b>∫</b> 0·3	
242)	<b>75</b> -40	95.36	1.0	[0·1	
601)	06.76	<b>96</b> •71	1.3	∫0·04	
004)	30.70	96-68	15	<b>[</b> 0·2	
431 <sub>a1</sub> ]	08.26	98-28	2.5 broad	<b>∫0</b> ∙8	
$104_{a_1}$	90-20	<b>98</b> ·25	2 5 61044	<b>[</b> 0·2	
$512_{a_1}$	100.26	100-29	4.8	∫0·1	
3 2 3 a)	100-20	100-28	40	<b>[0</b> ∙8	
$512_{\alpha_1}$	100.66	100.64	2.5	<b>∫0</b> ∙06	
323	100-00	100-63	2.5	<b>(0</b> ∙4	
$114_{\alpha_1}$	101-91	101.63	1.8 broad	0.3	
$214_{\alpha_1}$	108.56	108-52	3.5	<u>∫</u> 0·2	
$161_{\alpha_1}$	100.50	108-55	55	<b>\0</b> ∙6	
$602_{\alpha_1}$	109-06	108-90	3.5	0-3	
503 <sub>a</sub> ]	110.90	110.66	2.5	<u>∫</u> 0·4	
$432_{a}$	110.00	110.67	5.2	<b>[0</b> ∙3	
503.	111 10	111 <b>·07</b>	2.0	(0.2	
432	111.10	111.08	2.0	<b>[0</b> ∙2	
304	112-10	112.07	3.5	0.5	
304	112.60	112-49	2.0	0.3	
2 5 2 <sub>a1</sub>	114-25	114-27	3.5	0.9	
4 2 3 <sub>a1</sub>	116-05	116-09	3.5	0.6	
423	116.55 116.55		1.8	0.3	

Table 2. (Contd.)

	Observed*	Calculated <sup>†</sup>	Observed*	Calculated‡
hki	2θ (deg)	2θ (deg)	line intensity	line intensity
$2 2 4_{\alpha_1}$	117.60	117.57	1.8	0.4
$224_{a_2}$	118-20	118.04	1.0	0.2
701 <sub>a1</sub> ]		119.50		(0.3
$531_{\alpha_1}$	119-40	119-50	3.5	{0·7
$3 1 4_{\alpha_1}$		119-47		0.2
$513_{\alpha_1}$	121.90	121-80	4.0	<b>(0·8</b>
$6 1 2_{\alpha_1}$	121.00	121.81	4.0	<b>\0</b> ·2
$513_{a_2}$	122.40	122.31	2.0	<b>∫0</b> •4
$6 1 2_{\alpha_2}$	122.40	122.32	2.0	<b>ໄ0</b> ∙1
$404_{\alpha_1}$	125.30	125-38	3.5 brood	<b>∫</b> 0·2
621 <sub>α1</sub> ∫	145.59	125-41	5.5 010au	<b>[0</b> ∙7
710 <sub>a1</sub>	130-90	130.92	1.5	0.6
3 2 4 <sub>α1</sub>	131-80	131.77	1.5	0.3
4 4 2 <sub>a1</sub>	132.30	132-24	2.0	0.6
433 <sub>a1</sub>		134.52		(0.7
702 <sub>α1</sub> {	134.50	134-53	3.5	{ <b>0</b> ·2
532 <sub>α1</sub> J		134.53		(0.4
433az		135.20		0.4
702 <sub>02</sub> }	135-20	135.22	2.0	{0.09
$5 3 2_{\alpha_2}$		135-22		(0.2
$4 1 4_{\alpha_1}$	136-30	136-40	4.3	1.1
4 1 4 <sub>03</sub>	137-15	137.12	2.0	0.6
$450_{\alpha_1}$	140.39	140-46	1.3	{ <b>0</b> ∙05
$105_{\alpha}$		140-39		(0.4
$262_{\alpha_1}$	142.04	142.04	1.3	0.4
$5 4 1_{\alpha_1}$	147.29	147-22	3.0	1.1
$504_{a1}$		14/-1/		[0.3
800 <sub>a1</sub>	149.09	149.12	2.5	10.1
$205_{\alpha_1}$		149.03		[U·8 (0.05
800 <sub>a2</sub>	149-94	150.09	1.3	0.05
$203_{\alpha_2}$	151.00	150.00	4.0	(0.4
103 <sub>α1</sub>	151-07	157.21		1.7
$103_{\alpha_2}$	152-17	152.05	2.5 broad	0.0
554 <sub>α1</sub>	154.00	155-95	1.5 broad	0.0
554 <sub>α2</sub> 713	158.08	159.01	4-0 broad	2.0
$(12_{\alpha_1})$	130.30	160.60	TUUIUau	2·7 (1.6
$\frac{12_{\alpha_2}}{215}$	160.73	160.83	4.0 broad	1.0
$2 I J_{\alpha_1}$		100.03		(2.1

Table 2. (Contd.)

\*Two independent observers' averaged readings ( $2\theta$  readings are  $\pm 0.10^{\circ}$ ) and averaged intensities on a scale from ten to zero.

†Based on the hexagonal lattice parameters  $a_0 = 7.3817 A$ ,  $c_0 = 4.1274 A$  and  $\lambda(\hat{\alpha}) = 1.54178 A$ ,  $\lambda(\alpha_1) = 1.54051 A$ , and  $\lambda(\alpha_2) = 1.54433 A$ .

Calculated using the POWD intensity program[6] and scaled such that the most intense line had <math>I = 10.0.

Usually such a series of isomorphic compounds lends itself for calculation of the corresponding ionic radii; however, because of the anisotropies in this

<sup>6.</sup> D. K. Smith, University of California Lawrence Radiation Laboratory Rep. No. UCRL-7196 (1963).



Fig. 1. (a) and (b). Lattice parameters of the UCl<sub>3</sub>-type hexagonal actinide trichlorides.

trichloride series, the concept of ionic radius should be regarded with considerable caution. Radii calculations are based on averaged inter-atomic 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

Actinide trichloride	Lattice parameters (A)		M-Cl bond distances (A)		
	<i>a</i> <sub>0</sub>	<i>C</i> <sub>0</sub>	apical	equitorial	(CN = 6)
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

Table 3. Actinide-chloride bond distances and actinide trivalent ionic radii (derived from UCl<sub>3</sub>-type hexagonal actinide trichloride crystal data)

\*Calculated according to the following formula:

Ionic radius = [3(M-C)] equitorial bond distance)

+ 6(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].

7. W. H. Zachariasen, The Actinide Elements, Vol. 14A, Chap. 18. McGraw-Hill, New York (1954).

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 the 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<sub>3</sub>-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.

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