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Journal of Inorganic and Nuclear Chemistry

UCRL-16476

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

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ABSTRACT

$CmCl_3$ has been found to exhibit the hexagonal UCl_3 structure. Powder data from two samples give average lattice parameters $a = 7.380 \pm 0.006$A and $c = 4.186 \pm 0.010$A, where the error limits are the 95% confidence interval calculated using the standard statistical method for the average of two independent determinations.

INTRODUCTION

The crystal structure and lattice parameters of curium trichloride have been reported by Asprey, Keenan, and Kruse.[1]

The lattice parameters for curium trichloride calculated from data obtained by us are in serious disagreement with the work referred to above. Since tabulated values for the ionic radii of the tri-positive actinide ions have been derived largely from crystallographic data on the trichlorides, and since these radii are of value in predicting structures of a variety of compounds, we feel that it is of importance that the discrepancy in the curium trichloride data be resolved. We describe in some detail below the derivation of our experimental data, and the methods of calculation used to arrive at the lattice parameters.

EXPERIMENTAL

A. Materials

X-ray diffraction data were obtained on two samples of curium trichloride, derived from separate curium stock solutions which had been subjected to different purification procedures.

The starting material for the first sample consisted of a mixture of about 12 mg of Am^{243} and 12 mg of Cm^{244}, together with small amounts of common impurities such as Ca, Mg, Al, and Fe.

An americium-curium separation was achieved by two successive ion exchange elutions, using alphahydroxyisobutyric acid as the eluting agent.[2] The separated curium fraction was loaded onto Dowex 50 ion exchange

resin contained in a quartz tube and moved to the bottom of the resin bed column with 2 M HCl. Curium was then stripped from the resin using 6 M HCl, the eluate being collected in three fractions. A sixty-microgram sample of the 7.5 mg middle fraction was analyzed for impurities by spectrographic emission analysis using copper spark excitation. Limits of detection for various elements by this method have been given in a previous publication.(3) The only impurities detected in the 7.5 mg curium fraction were 0.04 atom percent americium, 0.16 atom percent silicon and 0.1 atom percent calcium.

About 40 micrograms of curium were taken from this stock and transferred to a quartz microcone. The hydrochloric acid solution was evaporated to dryness, treated with a few microliters of freshly distilled nitric acid, re-evaporated to dryness and heated in air to about 600°C.

A portion of the curium oxide obtained in this way was scraped free, using a platinum wire scraper, and transferred to a quartz x-ray capillary. The capillary was connected to a vacuum line and the oxide treated for about ten minutes with one-half atmosphere of $HCl_{(g)}$ at 400° C. Excess HCl and water vapor formed by the reaction were removed by pumping, after which fresh HCl was again added to the system. This process was repeated several times. In the final treatment the sample was allowed to cool to room temperature in the presence of HCl, which was then pumped off, and the capillary sealed for examination of the chloride by x-ray diffraction.

Diffraction lines from this preparation were recorded on Film 1500-A.

Starting material for the second trichloride sample was about 18 mg of Cm^{244} containing a small amount of americium together with significant amounts of Fe, Al, Ca, etc.

An americium-curium separation was effected by ion exchange, using Dowex 1 × 8 resin and 4.2 M $LiNO_3$ at pH 2.15 as eluting agent.[4]

The curium fraction from this column operation was treated with excess NH_4OH to precipitate $Cm(OH)_3$, which was washed several times and then dissolved in a minimum volume of 0.1 M HCl. The 0.1 M HCl solution was transferred to the top of a Dowex 50 × 4 resin bed contained in a quartz tube. The curium was then moved to the bottom of the resin column with 2 M HCl and stripped with 6 M HCl. This method is highly effective in separating curium from such common impurities as Al, Ca, and Fe.

A 24 μgm sample of the purified curium sample was analyzed by copper spark emission analysis. The only impurity detected was 0.42 atom percent of americium.

A few microliters of this curium stock solution were transferred to a clean platinum plate, evaporated to dryness, treated with 10 μl of freshly distilled nitric acid, re-evaporated and heated in air to 600° C. Subsequently the sample was re-heated in air in an open tube furnace for 10 minutes at 675° C.

After cooling, a portion of the curium oxide was transferred from the platinum plate to a quartz capillary and heated in a stream of anhydrous $HCl_{(g)}$ for 35 minutes at 400-500° C. The tip of the capillary was then sealed, the sample cooled to room temperature, excess HCl pumped off, and the capillary sealed.

The diffraction lines were recorded on Film 2069-A, using diffraction equipment described below.

B. Diffraction equipment

The diffraction equipment consisted of a Model 80-000 Jarrel-Ash Microfocus x-ray source and a 114 mm diameter Norelco Precision Powder Camera, manufactured by the Phillips Electronics Instrument Company.

RESULTS AND DISCUSSION

Line positions on Film 1500-A were read twice and averaged; those on 2069-A were read once.

Following indexing, the data were transferred to cards for 7094 computor determination of the most probable lattice parameter values, according to a least-squares fit of the differences between experimental $\sin^2\theta$ values and those calculated from the assigned indices. Two computational programs were used: the LCR-2 program developed by Williams[5] and the MET-124 program of Mueller and Heaton.[6]

Lattice parameters calculated by the two programs were the same to less than 0.001 A.

Line intensities were calculated theoretically, on the basis of the assumed UCl_3-type hexagonal structure, by using the POWD program developed by Smith.[7]

In Table 1 below we present a comparison of observed and calculated $\sin^2\theta$ values, as well as observed and calculated line intensities for both $CmCl_3$ preparations.

TABLE 1. OBSERVED AND CALCULATED INTENSITIES AND $\sin^2\theta$ VALUES FOR $CmCl_3$

			2069A		1500A	
	$\sin^2\theta$ (b)	I (c)	$\sin^2\theta$	I (d)	$\sin^2\theta$	I (d)
hkl	Calc.	Calc.	Obs.	Obs.	Obs.	Obs.
100 β	0.0119		0.0118	7	0.0118	7
100 $\bar{\alpha}$	0.0145	98	0.0146	10	0.0145	10
110 β	0.0356		0.0355	7	0.0357	4
101 β	0.0395		0.0397	8	0.0397	4
110 $\bar{\alpha}$	0.0436	66	0.0437	10	0.0436	8
101 $\bar{\alpha}$	0.0485	100	0.0486	10	0.0486	10
200 $\bar{\alpha}$	0.0582	23	0.0582	8.5	0.0582	4
111 β	0.0632		0.0635	2	0.0634	2
201 β	0.0751		0.0750	7	0.0748	4
111 $\bar{\alpha}$	0.0776	11	0.0777	4	0.0777	4
120 β	0.0830		0.0832	2	0.0831	2
201 $\bar{\alpha}$	0.0921	91	0.0920	10	0.0921	10
120 $\bar{\alpha}$	0.1018	16	0.1018	5.5	0.1017	4
300 β	0.1068		0.1066	4	0.1068	2.5
002 β	0.1106		0.1108	7	0.1107	4
121 β	0.1107					
102 β	0.1225		0.1228	1		-
300 $\bar{\alpha}$	0.1309	35	0.1307	8.5	0.1310	7
002 $\bar{\alpha}$	0.1357	16	0.1356	10	0.1359	10
121 $\bar{\alpha}$	0.1358	76				
220 β	0.1423		0.1423	1	0.1422	1
112 β	0.1462		0.1463	2	0.1463	2

TABLE 1. (Cont'd)

			2069A		1500A	
	$\sin^2\theta$ (b)	I (c)	$\sin^2\theta$	I (d)	$\sin^2\theta$	I (d)
hkl	Calc.	Calc.	Obs.	Obs.	Obs.	Obs.
102 $\bar{\alpha}$	0.1502	10	0.1503	4	0.1504	4
130 β	0.1542		0.1544	1	-	
202 β	0.1581		0.1582	1	-	
220 $\bar{\alpha}$	0.1746	14	0.1748	7	0.1746	4
112 $\bar{\alpha}$	0.1793	21	0.1794	8	0.1796	7
131 β	0.1819		0.1825	2	-	
130 $\bar{\alpha}$	0.1891	8	0.1893	7	0.1893	4
122 β	0.1936		0.1941	7	0.1941	4
202 $\bar{\alpha}$	0.1939	8				
302 β	0.2174		0.2177	2	0.2177	2.5
401 β	0.2174					
131 α_1	0.2227	15	0.2232	8	-	
131 $\bar{\alpha}$	0.2230	22	-		0.2233	7
131 α_2	0.2238	6	0.2239	4	-	
400 α_1	0.2324	3	0.2330	4	-	
400 $\bar{\alpha}$	0.2328	4	-		0.2328	2.5
212 α_1	0.2371	6	0.2374	5	-	
212 $\bar{\alpha}$	0.2375	9	-		0.2379	4
140 β	0.2491		0.2491	2	0.2492	2
222 β	0.2529		0.2532	4	0.2532	4
231 β	0.2530					
302 α_1	0.2662	15	0.2667	7	-	

TABLE 1. (Cont'd)

			2069A		1500A	
	$\sin^2\theta$ (b)	I (c)	$\sin^2\theta$	I (d)	$\sin^2\theta$	I (d)
hkl	Calc.	Calc.	Obs.	Obs.	Obs.	Obs.
401 α_1	0.2662	5	0.2674	4	-	
302 $\bar{\alpha}$	0.2666	23	-		0.2670	8
401 $\bar{\alpha}$	0.2667	7				
230 α_1	0.2760	3	0.2763	4	-	
230 $\bar{\alpha}$	0.2764	5	-		0.2761	4
203 β	0.2963		0.2968	2	0.2971	2
500 β	0.2965					
140 α_1	0.3050	9	0.3053	4	-	
140 $\bar{\alpha}$	0.3055	13	-		0.3058	5
140 α_2	0.3065	4	0.3062	2	-	
222 α_1	0.3097	7	0.3096	7		
231 α_1	0.3098	18				
222 $\bar{\alpha}$	0.3102	11	-		0.3108	9
231 $\bar{\alpha}$	0.3103	27				
222 α_2	0.3113	4	0.3117	4	-	
231 α_2	0.3114	9				
103 α_1	0.3193	5	0.3198	4		
103 $\bar{\alpha}$	0.3198	7	-		0.3195	4
132 α_1	0.3243	4	0.3242	4	-	
132 $\bar{\alpha}$	0.3248	7	-		0.3246	4
123 β	0.3319		0.3324	2	0.3319	2

TABLE 1 (Cont'd)

			2069A		1500A	
	$\sin^2\theta$	$I^{(c)}$	$\sin^2\theta$	$I^{(d)}$	$\sin^2\theta$	$I^{(d)}$
hkl	Calc.	Calc.	Obs.	Obs.	Obs.	Obs.
142 β	0.3597		0.3598	2	0.3597	2
241 β	0.3598					
203 α_1	0.3628	7	0.3637	4		
500 α_1	0.3631	1				
203 $\bar{\alpha}$	0.3634	11	-		0.3637	4
500 $\bar{\alpha}$	0.3637	2				
402 α_1	0.3678	3	0.3682	2	-	
402 $\bar{\alpha}$	0.3684	4	-		0.3687	2
501 α_1	0.3970	6	0.3976	4	-	
501 $\bar{\alpha}$	0.3976	10	-		0.3972	4
123 α_1	0.4064	9	0.4065	4	-	
123 $\bar{\alpha}$	0.4071	14	-		0.4072	7
123 α_2	0.4084	5	0.4082	2	-	
232 α_1	0.4114	4	0.4122	2	-	
142 α_1	0.4404	10	0.4406	7	-	
241 α_1	0.4405	7				
142 $\bar{\alpha}$	0.4412	15	-		0.4413	10
241 $\bar{\alpha}$	0.4413	10				
142 α_2	0.4426	5	0.4432	4	-	
241 α_2	0.4427	3				
233 β	0.4742		0.4749	2	-	
151 α_1	0.4841	8	0.4841	7	-	

TABLE 1 (Cont'd)

			2069A		1500A	
	$\sin^2\theta$ (b)	I (c)	$\sin^2\theta$	I (d)	$\sin^2\theta$	I (d)
hkl	Calc.	Calc.	Obs.	Obs.	Obs.	Obs.
151 $\bar{\alpha}$	0.4849	11	-		0.4846	5
151 α_2	0.4865	4	0.4867	4	-	
133 α_1	0.4935	5	0.4937	4	-	
133 $\bar{\alpha}$	0.4944	7	-		0.4946	4
600 α_1	0.5229	2	0.5237	0.5	-	
332 α_1	0.5276	4	0.5277	2	-	
332 $\bar{\alpha}$	0.5285	6	-		0.5272	3
403 α_1	0.5371	2	0.5373	4	-	
340 α_1	0.5374	2				
403 $\bar{\alpha}$	0.5380	3	-		0.5371	4
340 $\bar{\alpha}$	0.5383	2				
?	?	?	a		0.5498	
?	?	?	a		0.5566	
250 α_1	0.5664	5	0.5663	2	-	
341 α_1	0.5713	5	0.5706	2	-	
341 $\bar{\alpha}$	0.5722	8	-		0.5710	4
341 α_2	0.5741	3	0.5741	2	-	
233 α_1	0.5807	8	0.5806	7	-	
233 $\bar{\alpha}$	0.5816	12	-		0.5808	5
233 α_2	0.5836	4	0.5841	4	-	
114 $\bar{\alpha}$	0.5863	4	-		0.5851	2
512 $\bar{\alpha}$	0.5867	2				

TABLE 1 (Cont'd)

			2069A		1500A	
	$Sin^2\theta$ (b)	I (c)	$Sin^2\theta$	I (d)	$Sin^2\theta$	I (d)
hkl	Calc.	Calc.	Obs.	Obs.	Obs.	Obs.
204 $\bar{\alpha}$	0.6008	2	-		0.6014	2
153 β	0.6166		-		0.6169	2
124 $\bar{\alpha}$	0.6445	3	-		0.6447	2
602 α_1	0.6583	3	0.6585	7	0.6577	4
161 α_1	0.6584	5				
602 α_2	0.6616	1	0.6618	4	0.6620	2
161 α_2	0.6617	3				
503 α_1	0.6678	4	0.6679	4	0.6681	2
304 α_1	0.6725	5	0.6725	7	0.6727	4
342 α_1	0.6728	3				
304 α_2	0.6758	3	0.6766	4	0.6759	2
342 α_2	0.6762	1				
440 α_1	0.6972	2	0.6976	1	-	
252 α_1	0.7019	9	0.7019	7	0.7023	4
252 α_2	0.7054	4	0.7056	4	-	
243 α_1	0.7114	5	0.7115	7	0.7115	4
243 α_2	0.7149	3	0.7151	5	-	
224 α_1	0.7160	3	-		0.7162	4
134 α_1	0.7306	5	-		0.7312	2
351 α_1	0.7455	7	0.7456	4	0.7458	4
351 α_2	0.7493	3	0.7491	2	-	

TABLE 1 (Cont'd)

			2069A		1500A	
	$\sin^2\theta$ (b)	I (c)	$\sin^2\theta$	I (d)	$\sin^2\theta$	I (d)
hkl	Calc.	Calc.	Obs.	Obs.	Obs.	Obs.
153 α_1	0.7550	7	0.7551	5	0.7553	5
260 α_1	0.7553	2				
153 α_2	0.7587	4	0.7592	4	0.7593	4
260 α_2	0.7590	1				
404 α_1	0.7741	2	0.7747	2	0.7752	2
261 α_1	0.7891	6	0.7891	7	0.7888	4
261 α_2	0.7930	3	0.7933	4	-	
234 α_1	0.8177	3	-		0.8180	2
170 α_1	0.8279	6	0.8279	2	0.8282	2
170 α_2	0.8320	3	0.8328	4	0.8328	4
442 α_1	0.8326	6				
442 α_2	0.8367	3	0.8366	2	-	
343 α_1	0.8421	7	0.8422	2	0.8423	2
343 α_2	0.8463	3				
144 α_1	0.8467	10	0.8466	7	0.8475	7
352 α_1	0.8471	4				
144 α_2	0.8510	5	0.8512	4	0.8516	4
352 α_2	0.8513	2				
262 α_1	0.8907	4	0.8907	2	0.8911	2
205 α_1	0.9046	7	0.9044	7	0.9050	5
504 α_1	0.9048	3				

TABLE 1 (Cont'd)

			2069A		1500A	
	$\sin^2\theta$ (b)	I (c)	$\sin^2\theta$	I (d)	$\sin^2\theta$	I (d)
hkl	Calc.	Calc.	Obs.	Obs.	Obs.	Obs.
205 α_2	0.9091	4	0.9090	2	-	
504 α_2	0.9093	1				
360 α_1	0.9150	5	0.9151	2	-	
360 α_2	0.9196	3	0.9194	7	-	
451 α_1	0.9198	11			0.9204	4
163 α_1	0.9293	11	0.9290	7	0.9297	5
163 α_2	0.9339	4	0.9334	7	0.9343	5
334 α_1	0.9339	7				
125 α_1	0.9481	14	0.9478	7	0.9486	7
125 α_2	0.9528	8	0.9529	4	0.9535	4
172 α_1	0.9633	27	0.9630	7	0.9635	7
801 α_1	0.9634	8				
172 α_2	0.9681	14	0.9680	4	0.9686	4
801 α_2	0.9682	4				

TABLE 1 (Cont'd)

[a]The two unindexable trace lines at $\sin^2\theta$ equal to 0.5498 and 0.5566 were independently observed only on film 1500A. On re-examination of film 2069A, these features were definitely located; however, the intensities of the reflections were very low.

[b]Calculated using a = 7.380A and c = 4.186A with $\lambda_{\bar{\alpha}}$ = 1.54178A, λ_{α_1} = 1.54051A, λ_{α_2} = 1.54433A and λ_β = 1.39217A.

[c]Calculated using the POWD intensity program assuming the atomic coordinates of UCl_3 and scaled such that the strongest line has an intensity of 100.

[d]Estimated visually relative to a value of 10 for the strongest line.

The following features of the data recorded in Table 1 should be noted:

1) All lines except two appearing on each film have been indexed and included in the computation of the lattice parameters.

2) The two unassigned lines appear at barely detectable intensity.

3) The quality of film 2069A is superior to that of 1500A in the sense that the pattern is clearer (α_1 - α_2 separations are noted at $\sin^2\theta$ = 0.223 in 2069A as compared with $\sin^2\theta$ = 0.660 in 1500A).

4) For either film the greatest difference between an observed and a calculated $\sin^2\theta$ is 0.0013.

5) There are no significant discrepancies between observed and calculated intensities for either film.

6) Lattice parameters calculated for the two preparations are the same within 0.001A.

7) From film 2069A the observed lattice parameters are calculated to be $a = 7.3803 \pm 0.0002A$ and $c = 4.1862 \pm 0.0002A$, while those from film 1500A are: $a = 7.3793 \pm 0.0003A$, $c = 4.1847 \pm 0.0002A$. The above error limits are standard deviations for the individual patterns computed using the LCR-2 program. Drs. Asprey and Keenan have been kind enough to inform[8] us that the films on which their computations were based were of relatively poor quality and exhibited no lines having diffracting angles above 45°. These facts probably account for the differences between their calculated parameters and ours.

The interval agreement of the powder data is consistent with error limits of ±0.001A for both lattice parameters. The use of these limits is in accordance with customary practice. From a chemical standpoint, however, it is suggested that error limits based entirely on the agreement of independent determinations would be more meaningful. Treating the results presented here as two independent determinations of the lattice parameters, the application of standard statistical methods to the average, accounting for nonstatistical sampling, gives for the 95% confidence interval:

$$a = 7.380 \pm 0.006A \qquad c = 4.186 \pm 0.010A$$

This provides a statistically meaningful basis for comparison with other groups of independent determinations. It is felt that information of this sort would be of great assistance in the recognition of anomalies due to the effect of purity, nonstoichiometry, radiation damage, etc.

ACKNOWLEDGMENTS

We wish to express our thanks to Miss Lilly Goda for assistance in sample preparation and film reading, Mrs. Gertrude Boltz for radiation monitoring, and Mr. George Shalimoff for spectrographic analyses.

FOOTNOTES AND REFERENCES

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

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