Title

CRYSTALLOGRAPHY OP THE COMPOUNDS OF CALIFORNIUM. I. CRYSTAL STRUCTURE AND LATTICE PARAMETERS OF CALIFORNIUM SESQUIOXIDE AND CALIFORNIUM TRICHLORIDE

Authors

Green, J.L.
Cunningham, B.B.

Publication Date

1967-05-09

UCRL-17539

cy. 2

University of California

Ernest O. Lawrence Radiation Laboratory

CRYSTALLOGRAPHY OF THE COMPOUNDS OF CALIFORNIUM. I. CRYSTAL STRUCTURE AND LATTICE PARAMETERS OF CALIFORNIUM SESQUIOXIDE AND CALIFORNIUM TRICHLORIDE

J. L. Green and B. B. Cunningham

May 9, 1967

Berkeley, California

DISCLAIMER

Submitted to Inorg. and Nucl. Chem. Letters

UCRL-17539
Preprint

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

CRYSTALLOGRAPHY OF THE COMPOUNDS OF CALIFORNIUM. I. CRYSTAL STRUCTURE AND LATTICE PARAMETERS OF CALIFORNIUM SESQUIOXIDE AND CALIFORNIUM TRICHLORIDE

J. L. Green and B. B. Cunningham

May 9, 1967

UCRL-17539

CRYSTALLOGRAPHY OF THE COMPOUNDS OF CALIFORNIUM. I. CRYSTAL STRUCTURE AND LATTICE PARAMETERS OF CALIFORNIUM SESQUIOXIDE AND CALIFORNIUM TRICHLORIDE*

J. L. Green† and B. B. Cunningham

Department of Chemistry and Lawrence Radiation Laboratory

University of California, Berkeley, California

Introduction

The work reported below is part of a continuing program of investigation of the crystallographic properties of compounds of the 5f transition elements and constitutes the first such studies on californium.

Experimental

A. Materials

The ~ 360 day alpha-emitting isotope of californium of mass 249 was used. It was purified on a microgram scale by standard ion exchange methods (1,2,3,4) using specially purified reagents and ion exchange materials (5).

The purified californium was absorbed to saturation on single beads of Dowex 50 AG × 4 resin in 0.2 and 0.5 μgm quantities.

Tests to determine the purity of the californium included pulse analysis for Pu, Am and Cm, and mass analysis for Nd (as an indication of rare earth contamination). Actinides were not detected at limits of about one atom percent.

---

*The work reported was done in partial satisfaction of the requirements for the Ph. D. degree in Chemistry, University of California, Berkeley

†CMB-11, Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87544

Mass analysis revealed the presence of 0.32 atom percent of neodymium. Although it was not possible to analyze the californium for all possible impurities, significant contamination seems unlikely on the basis of the purification procedures used and its inconsistency with the crystallographic data.

B. Procedure

The ion exchange beads containing californium were ignited at ~ 1200° C to produce the oxide, which was then transferred to quartz x-ray capillary tubes. This technique for preparing x-ray samples has been described in previous publications (6,7).

Oxide contained in the capillaries was treated at 600° C with dry hydrogen gas at one-half atomosphere pressure and then cooled in hydrogen. The resulting material was pale yellow in color. Conversion of the oxide to trichloride was accomplished by treating the oxide in situ with anhydrous HCl at 520° C for three ten-minute periods interrupted by cooling, evacuation and admission of fresh HCl.

In one preparation the furnace temperature rose to 600°, melting the sample. Examination of the cooled product by optical microscopy indicated the formation of a single crystal. Visually, this sample was transparent, with a clear emerald-green color.

Subsequent preparations at 520° yielded polycrystalline specimens which produced satisfactory powder diagrams.

Powder patterns were obtained with a Model 80-000 Jarrell-Ash Microfocus x-ray source and Phillips-Norelco powder cameras of 57.3 mm diameter. Exposure times were 15-20 hours.

Diffraction lines on each film were read independently by two observers and the θ values averaged. The patterns were then indexed by comparison with data available on isostructural compounds and through the use of $\sin^2 \theta$ data and intensity calculations performed according to the POWD computer program developed by D. K. Smith (8).

The lattice parameters were computed by least squares fitting of the $\sin^2 \theta$ data using the LCR-2 program developed by D. E. Williams (9).

Results

A. Californium sesquioxide

Diffraction data were obtained from three separate Cf_2O_3 preparations. A portion of those derived from one sample are given in Table 1. Reference (5) gives data to $\sin^2 \theta = 0.9281$.

TABLE 1

Partial Line List and Indexing for Monoclinic Californium Sesquioxide Film 2363A

hkl	$\sin^2 \theta$ Calculated[a]	$\sin^2 \theta$ Observed	Intensity Calculated[b]	Intensity Observed[c]
111	0.0588	0.0589	8.0	10
401	0.0642	0.0641	8.5	9
$40\bar{2}$	0.0668	0.0665	9.1	9
003	0.0712	0.0711	6.4	8
310	0.0738	0.0736	10.0	9
$11\bar{2}$	0.0773	0.0773	9.5	10
600	0.1108	0.1106	1.2	4
$51\bar{1}$	0.1221	0.1221	1.9	5
$31\bar{3}$	0.1291	0.1287	4.3	7.5
313	0.1609	0.1609	5.4	7.5
020	0.1843	0.1836	2.8	6
$80\bar{1}$	0.1907	0.1908	1.6	4.5
$71\bar{2}$	0.2038	0.2037	3.5	6.5
404	0.2041		1.1	

[a] Calculated using a = 14.124 A; b = 3.591 A; c = 8.809 A; β = 100.31 degrees with $\lambda(\bar{\alpha})$ = 1.54178 A.

[b] Calculated using the POWD intensity program assuming the atomic coordinates of Sm_2O_3. The calculation was scaled such that the most intense line had an intensity of 10.0.

[c] Estimated visually on a scale from 10 to 1.

Lattice parameters calculated for all three preparations are given in Table 2 below.

TABLE 2

Californium Sesquioxide Lattice Parameters-Monoclinic Sm_2O_3 Structure

Film number	a (A)	$2\sigma a$ [a] (A)	b (A)	$2\sigma b$ [a] (A)	c (A)	$2\sigma c$ [a] (A)	β (deg.)	$2\sigma\beta$ [a] (deg.)
2338A	14.132	0.011	3.592	0.002	8.811	0.007	100.31	0.07
2363A	14.122	0.008	3.591	0.002	8.807	0.006	100.32	0.06
2382A	14.116	0.008	3.590	0.001	8.808	0.005	100.31	0.05
average [b]	14.124 ±	0.020	3.591 ±	0.003	8.809 ±	0.013	100.31 ±	0.02

[a] Estimated standard deviation for the individual preparations as computed from least squares fits using the LCR-2 lattice parameter program.

[b] The error limits placed on the average values were computed using

$$95\%\ \text{confidence error limit} = \frac{4.30}{\sqrt{N}}\sqrt{\frac{\Sigma d_i^2}{N-1}}$$

where d_i is the deviation of the individual lattice parameters from the average; N is the number of observations, i.e., 3; and the factor 4.30 is the 95% confidence Student t value for 3 observations.

B. Californium trichloride

Diffraction data were recorded from two californium trichloride samples. Least squares lattice parameters were a = 7.390 A, c = 4.095 A, a = 7.396 A, c = 4.085 A for the two samples, respectively. Applying the appropriate t value for two observations gives ±0.04 A and ±0.06 A for the 95% confidence interval for the average values of the a and c parameters, respectively.

Table 3 presents a comparison between observed and calculated $\sin^2 \theta$ and intensity values for one sample, using the two-sample average for a and c. Higher angle data up to $\sin^2 \theta = 0.9684$ are given in reference (5).

TABLE 3

Partial Line List and Indexing for Hexagonal Californium Trichloride Film 2430A

hkl	$\sin^2 \theta$ Calculated[a]	$\sin^2 \theta$ Observed	Intensity Calculated[b]	Intensity Observed[c]
101	0.0500	0.0501	10.0	10
200	0.0580	0.0580	2.4	7
111	0.0790	0.0788	1.0	4.5
201	0.0935	0.0932	9.2	10
210	0.1015	0.1010	1.5	5
300	0.1305	0.1302	3.6	8.5
121	0.1370	0.1373	7.7	10
002	0.1421	0.1425	1.5	5
102	0.1566	0.1575	1.0	5
220	0.1740	0.1736	1.4	5.5
112	0.1856	0.1860	2.1	8
202	0.2001	0.2001	0.8	4.5
131	0.2240	0.2236	2.4	8
400	0.2320	0.2306	0.4	3
212	0.2436	0.2435	0.8	4.5

[a] Calculated using a = 7.393 A and b = 4.090 A with λ = 1.54178 A.

[b] Calculated using the POWD intensity program assuming the atomic coordinates of UCl_3. The calculation was scaled such that the strongest line had an intensity of 10.0.

[c] Estimated visually on a scale from 10 to 1.

Discussion

Californium sesquioxide as prepared by the method described in this paper exhibits the monoclinic, B-type rare earth sesquioxide structure observed in high-temperature preparations of the sesquioxides of samarium and europium (10). We have calculated the ionic radius of Cf^{3+} to be 0.976 A from our data on $CfCl_3$, using the method of Zachariasen (11), who gives 0.97 A for the radius of Sm^{3+}. If the cation radius governs polymorphism in the sesquioxides of the 4f and 5f transition elements, then the occurrence of a high-temperature B-type sesquioxide in the californium is to be expected. (Since the work described above was completed, cubic Cf_2O_3 has been observed as a product of the hydrolysis of CfOCl at 600-700° (12), thus extending the crystallographic analogy between Cf_2O_3 and Sm_2O_3.)

We wish to point out, however, that the exact stoichiometry of our californium sesquioxide is not known.

Further, we would like to emphasize that the concept of ionic radius should be used with considerable caution, particularly as applied to compounds of different structure type. Even in compounds of the same structure type, internal consistency may be lacking. This is shown in Fig. 1 where we have plotted nearest-neighbor cation-chloride distances for the UCl_3-type structure compounds of the actinides.

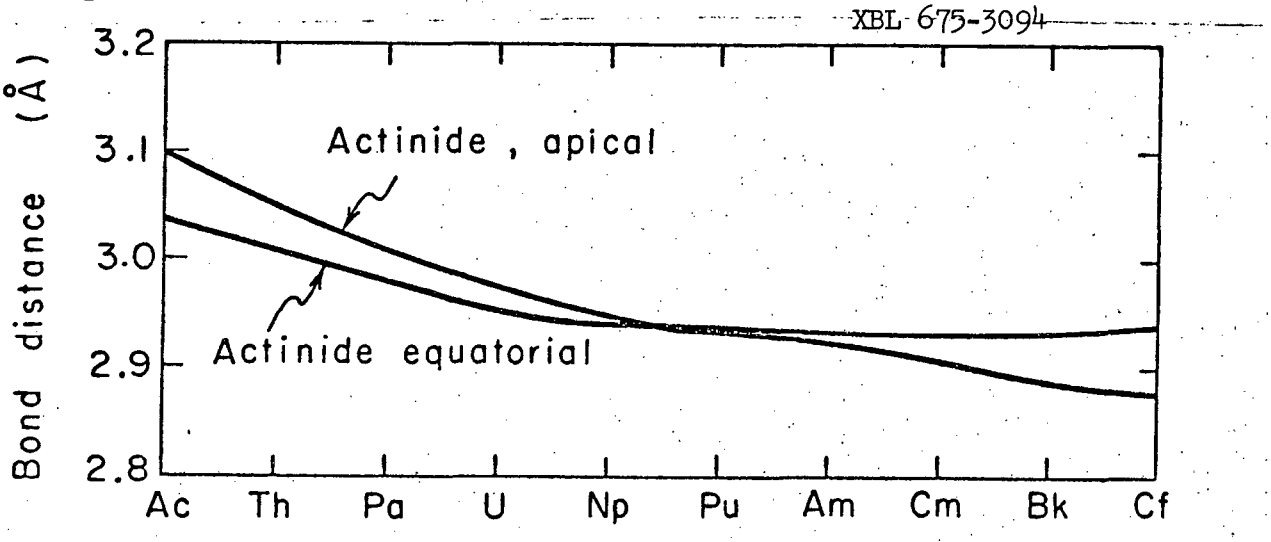

FIG. 1
M-Cl bond distances in the UCl_3-type actinide trichlorides.

From neptunium onward, the "actinide contraction" is confined almost exclusively to the bonds between the cation and the nearest-neighbor apical chlorides; metal-equatorial chloride distances are virtually constant, but show an actual increase between curium and californium.

The lanthanide trichlorides exhibiting the UCl_3-type structure show a similar anisotropic "lanthanide contraction."

Acknowledgement

The authors are deeply grateful to J. R. Peterson for assistance in film reading and data processing, to Dr. Maynard Michel for mass analyzing our samples, and to Mrs. Gertrude Bolz for performing the radiation monitoring essential for the safe performance of the experiments.

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

References

(1) J. P. SURLS, JR., Lawrence Radiation Laboratory Report, UCRL-3209 (1956).

(2) R. M. DIAMOND, K. STREET, JR., and G. T. SEABORG, J. Am. Chem. Soc. 76, 1461 (1954).

(3) K. STREET, JR. and G. T. SEABORG, J. Am. Chem. Soc. 72, 2790 (1950).

(4) G. R. CHOPPIN, B. G. HARVEY, and S. G. THOMPSON, J. Inorg. Nucl. Chem. 2, 66 (1956)

(5) J. L. GREEN, Ph. D. thesis, Lawrence Radiation Laboratory Report, UCRL-16516, November 1965.

(6) B. B. CUNNINGHAM, Microchemical Journal, Symposium (1961).

(7) B. B. CUNNINGHAM, Proceedings of the Robert A. Welch Foundation, Conferences on Chemical Research, VI, Topics in Modern Inorganic Chemistry, 1962.

(8) D. K. SMITH, Lawrence Radiation Laboratory Report, UCRL-7196 (1963).

(9) D. E. WILLIAMS, Ames Laboratory Report, IS-1052 (1964).

(10) R. S. ROTH and S. J. SCHNEIDER, J. Res. N. B. S., 64, 309 (1960).

(11) W. H. ZACHARIASEN, Chapter 18, Vol 14A, Plutonium Project Record, National Nuclear Energy Series, McGraw-Hill, New York, 1954.

(12) J. C. COPELAND and B. B. CUNNINGHAM, Unpublished.