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Authors
Templeton, D.H.
Dauben, Carol H.

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D. H. Templeton and Carol H. Dauben

February 3, 1953

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CRYSTAL STRUCTURES OF AMERICIUM COMPOUNDS[1]

D. H. Templeton and Carol H. Dauben
Department of Chemistry and Radiation Laboratory
University of California, Berkeley, California

February 3, 1953

ABSTRACT

The crystal structures of several compounds of americium, element 95, have been determined by the X-ray powder diffraction method. AmF_3 is hexagonal (LaF_3 type) with

$$\underline{a} = 4.067 \pm 0.001\ \text{Å}$$

and

$$\underline{c} = 7.225 \pm 0.002\ \text{Å}$$

for the pseudocell which explains the powder data. AmO_2 is cubic (CaF_2 type) with

$$\underline{a} = 5.383 \pm 0.001\ \text{Å}$$

AmOCl is tetragonal (PbFCl type) with

$$\underline{a} = 4.00 \pm 0.01\ \text{Å},$$

$$\underline{c} = 6.78 \pm 0.01\ \text{Å}.$$

The metal parameter is 0.18 ± 0.01. Am_2O_3 is cubic when prepared at 600° C. and hexagonal when prepared at 800° C. For the cubic form (Mn_2O_3 type)

$$\underline{a} = 11.03 \pm 0.01\ \text{Å}.$$

The metal parameter is -0.030 ± 0.002. For the hexagonal form (La_2O_3 type)

$$\underline{a} = 3.817 \pm 0.005\ \text{Å},$$

$$\underline{c} = 5.971 \pm 0.010\ \text{Å}.$$

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[1] This research was performed under the auspices of the AEC.

CRYSTAL STRUCTURES OF AMERICIUM COMPOUNDS

D. H. Templeton and Carol H. Dauben
Department of Chemistry and Radiation Laboratory
University of California, Berkeley, California

February 3, 1953

In cooperation with Professor B. B. Cunningham and his students, we have been observing the x-ray diffraction patterns of various compounds of americium, element 95. The isolation of americium produced by the beta decay of Pu^{241} has been described by Cunningham.[2] Prior to 1948 the purification was usually terminated when the impurities (chiefly lanthanum) were reduced to one or two percent. Since that time there have been available americium stocks of much higher purity.[3,4] In this paper we report our results concerning the crystal structures of AmF_3, AmO_2, AmOCl, and two forms of Am_2O_3.

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(2) B. B. Cunningham, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 19.2, McGraw-Hill Book Co., Inc., New York, N. Y., 1949.

(3) H. R. Lohr and B. B. Cunningham, J. Am. Chem. Soc. 73, 2025-28 (1951).

(4) L. Eyring, H. R. Lohr, and B. B. Cunningham, J. Am. Chem. Soc. 74, 1186-90 (1952).

Americium Trifluoride

Americium trifluoride was prepared by Dr. L. Eyring as described elsewhere.[5] Sample A (Table I) was pink in color, like that described by Fried.[6] Sample B was a subsequent preparation which was grey or lavender in color. Its diffraction pattern was almost identical with that of Sample A. Sample C was prepared by Dr. J. C. Wallmann from the very pure americium nitrate solution used by Howland and Calvin for their magnetic investigation.[7] Some of this americium was precipitated as the hydroxide and heated with oxygen to 525° C. It was then heated in hydrogen fluoride to 715° C. The product was pink but after a week, part of it had turned yellow. Sample C consisted of some of this yellow material.

With each of the three samples an excellent powder diffraction pattern was obtained corresponding to the LaF_3-type structure.[8]

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[5] E. G. Westrum and L. Eyring, J. Am. Chem. Soc. 73, 3396-98 (1951).

[6] S. Fried, J. Am. Chem. Soc. 73, 416-18 (1951).

[7] J. J. Howland and M. Calvin, J. Chem. Phys. 18, 239-43 (1950).

[8] I. Oftedal, Z. physik. Chem. B 5, 272-91 (1929); B 13, 190-200 (1931).

The unit cell dimensions listed in Table I refer to the hexagonal pseudo-cell containing two americium atoms. This cell accounts for all the diffraction lines observed in the powder patterns. Faint reflections in single crystal patterns[8,9] require an a axis which is $\sqrt{3}$ times as large as those listed in Table I. Zachariasen[10,11] first observed this structure for americium trifluoride and has reported two sets of cell dimensions based on samples of uncertain purity. His results (corrected from kX units) are included in the table. Our three samples disagree by only slightly more than the estimated limits of error. Since the material prepared by Wallmann is likely to be of the highest purity, we adopt as our best values a = 4.067 Å and c = 7.225 Å for the pseudo-cell. For the larger cell, a = 7.044 Å. The change from Zachariasen's values is not sufficient to affect his ionic radius for Am^{+3}, 0.99 Å.[12] We attach no structural significance to the color changes but attribute them to surface effects of some kind.

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(9) We have observed these weak reflections for a single crystal of pure synthetic CeF_3, showing that the effect in tysonite[8] is not due to ordering between the cerium and lanthanum atoms.

(10) W. H. Zachariasen, Phys. Rev. **73**, 1104-5 (1948).

(11) W. H. Zachariasen, Acta Cryst. **2**, 388-90 (1949).

(12) W. H. Zachariasen, American Crystallographic Association, Abstracts of Meeting, Pennsylvania State College, April 10-12, 1950.

Table I

Unit Cell Dimensions for Americium Trifluoride

Sample	a (Å)	c (Å)
A[a]	4.069 ± 0.001	7.229 ± 0.002
B[a]	4.069 ± 0.001	7.229 ± 0.002
C[a]	4.067 ± 0.001	7.225 ± 0.002
Zachariasen[10, b]	4.078 ± 0.002	7.239 ± 0.004
Zachariasen[11, b]	4.081 ± 0.002	7.245 ± 0.004

a Based on Cu K α, $\lambda = 1.5418$ Å.

b Corrected from kX units.

Americium Dioxide

The black americium dioxide was shown by Zachariasen to have the fluorite type structure.[10, 11] For samples of uncertain purity, the edge of the cubic unit cell was found to be 5.372 ± 0.005 kX and 5.377 ± 0.003 kX. We have examined by x-ray diffraction several americium dioxide samples, three of which were especially well crystallized and gave excellent powder patterns. Sample A (Table II) was prepared by Dr. L. B. Asprey by ignition of the nitrate in air. The americium stock which was used may have contained a few per-cent lanthanum. Sample B was prepared by Eyring from a much purer americium stock by heating the oxalate in air.[4] Some of this material subsequently was heated in a small quartz bomb to 500° C. with oxygen at 90 atm. pressure; the product is designated as sample C.

The values observed for the unit cell dimension are compared in Table II. The results for samples B and C show that the high pressure oxidation produces no significant change in the composition of this phase. Using the purer americium stock, Asprey and Cunningham[13] measured the amount of oxygen absorbed by americium sesquioxide when heated in oxygen. The result corresponds to AmO_x for the formula of the dioxide, with $x = 1.98 \pm 0.02$, if Am_2O_3 is the correct composition of the sesquioxide. Thus the "black dioxide" has very nearly the ideal composition, rather than an intermediate composition like the so-called Pr_6O_{11}.

The deviation of sample A from samples B and C, though small, is outside the experimental precision. The difference corresponds

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(13) L. B. Asprey and B. B. Cunningham, to be published.

to an oxygen defect in sample A of 0.01 O per Am, estimated from the data of McCullough[14] for rare earth oxide systems. This defect could be the result of an impurity of about 4 atomic percent of a trivalent rare earth element (probably lanthanum) in sample A.

Table II

Unit Cell Dimension of Americium Dioxide

Sample	a (Å)
A	5.387 ± 0.001[a]
B	5.383 ± 0.001
C	5.383 ± 0.001
Zachariasen[10]	5.383 ± 0.005[ab]
Zachariasen[11]	5.388 ± 0.003[ab]

[a] Purity uncertain.

[b] Corrected from kX units.

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(14) J. D. McCullough, J. Am. Chem. Soc. 72, 1386-1390 (1950).

Americium Oxychloride

Americium oxychloride was prepared by Dr. L. B. Asprey by accidental contamination in an experiment designed to yield the sesquioxide by hydrogen reduction of the dioxide. It was identified by its powder diffraction pattern which corresponded to the PbFCl type structure,[15] with the tetragonal unit cell dimensions $a = 4.00 \pm 0.01$ Å, $c = 6.78 \pm 0.01$ Å. A second sample was prepared by C. W. Koch by heating Am_2O_3 at 500° C. in a mixture of HCl and H_2O vapor. The pattern again corresponded to the unit cell dimensions listed above.

The atoms are located in the following special positions of space group D_{4h}^{7} -- *P4/nmm*:

2 Am in (c) : 0, 1/2, u; 1/2, 0, $\bar{u}$
2 Cl in (c) : 0, 1/2, v; 1/2, 0, $\bar{v}$
2 O in (a) : 0, 0, 0; 1/2, 1/2, 0

Comparison of observed with calculated intensities showed that $u = 0.18 \pm 0.01$. The intensities are not very sensitive to the value of v. We choose $v = 0.65$ so that the Cl--O and Cl--Cl distances are in the ratio of the sums of the ionic radii. In Table III are listed observed and calculated intensities. No corrections for temperature or absorption have been made. In this structure each americium ion has four oxygen neighbors at 2.34 Å, four chlorine neighbors at 3.05 Å, and one chlorine at 3.18 Å.

Zachariasen[11] gives $u = 0.18$ and $v = 0.64$ for the isostructural compound PuOCl.

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(15) W. Nieuwenkamp and J. M. Bijvoet, Z. Krist. **81**, 469-474 (1931).

Table III

Powder Diffraction Data for AmOCl

$hk\ell$	$\sin^2\theta$		intensity	
	obs.	calc.	obs.	calc.
001	---a	0.0129	---a	17
101	0.0501	0.0501	vs+	$55\left\{\begin{matrix}48\\7\end{matrix}\right.$
002		0.0516		
110	0.0746	0.0743	s	30
111	0.0891	0.0872	vs	$37\left\{\begin{matrix}3\\34\end{matrix}\right.$
102		0.0887		
003	0.1163	0.1162	vw	4
112	0.1268	0.1259	m-	13
200	0.1493	0.1486	m	14
103	---	0.1538	---	1
201	0.1609	0.1615	vw	3
113	0.1913	0.1905	m-	11
211	0.1996	0.1987	m+	16
004	---	0.2068	---	0.2
212	0.2380	0.2374	m+	15
104	0.2438	0.2437	w	10

[a] Not on film.

Americium Sesquioxide

Americium sesquioxide was prepared by Eyring[4] by heating the black dioxide in 1/3 atmosphere of hydrogen at about 600° C. for half an hour. The product was a reddish brown (persimmon) color. It was first identified by its x-ray diffraction pattern, which corresponded to the cubic Mn_2O_3 type[16] structure, with the cell constant equal to 11.03 ± 0.01 Å. Subsequent experiments by Asprey and Cunningham[13] confirmed its composition.

Another americium oxide was prepared by Carniglia[17] by the ignition of the oxalate at 850° C., followed by reduction with 1/6 atmosphere of hydrogen at about 800° C. The resulting pale tan material was identified as Am_2O_3 by its diffraction pattern which corresponded to the hexagonal La_2O_3 type structure.[18]

The dimensions of the unit cell are:

$$\underline{a} = 3.817 \pm 0.005 \text{ Å}$$
$$\underline{c} = 5.971 \pm 0.010 \text{ Å}$$

A few weak lines are attributed to some unidentified impurity.

For the mineral bixbyite, $(Fe, Mn)_2O_3$, which is isostructural with the cubic Am_2O_3, Pauling and Shappell[16] give the atomic

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(16) L. Pauling and M. D. Shappell, Z. Krist. 75, 128-42 (1930).

(17) S. Carniglia, unpublished work.

(18) L. Pauling, Z. Krist. 69, 415-21 (1929).

positions as:

Space group T_h^7--Ia3

32 metal atoms in (0, 0, 0; 1/2, 1/2, 1/2) +

8b: (1/4, 1/4, 1/4; 1/4, 3/4, 3/4; ↻)

24d: ± (u, 0, 1/4; ↻ ; $\bar{u}$, 1/2, 1/4; ↻) with u = -0.030 ± 0.005

48 oxygen atoms in (0, 0, 0; 1/2, 1/2, 1/2) +

48e: ± (x, y, z; ↻ ; x, $\bar{y}$, 1/2 - z; ↻ ; 1/2-x, y, $\bar{z}$; ↻ ;
$\bar{x}$, 1/2 - y, z; ↻)

with x = 0.385 ± 0.005
y = 0.145 ± 0.005
z = 0.380 ± 0.005

The observed intensities of the cubic Am_2O_3 pattern, when compared with those calculated for various values of the parameter u, fix that parameter as -0.030 ± 0.002, in exact agreement with the result for bixbyite. This agreement is an excellent confirmation of the previous work, since the calculations for the americium compound are little influenced by the positions chosen for oxygen. The lines most useful in the determination of the parameter were those with $h^2 + h^2 + \ell^2$ equal to 38, 46, 48, 62, and 64. In Table IV are listed the observed intensities for the cubic Am_2O_3 and those calculated for the parameter values listed above for bixbyite. No correction was made for temperature or absorption. It should be noted that in general ($hk\ell$) and (ℓkh) have different structure factors. In this structure, each americium atom is surrounded by six oxygen atoms at a distance of 2.36 Å.

No intensity calculations have been carried out for the hexagonal Am_2O_3, but the similarity of the observed intensities

Table IV

Powder Diffraction Data for Cubic Am_2O_3

$h^2+k^2+\ell^2$	I. obs.	I calc.
12	vs	167
14	vw	6
16	s-	79
18	w	9
20	--	1
22	vw	4
24	--	1
26	m-	12
30	vw	3
32	s	62
34	vw	4
36	--	1
38	w	8
40	--	2
42	vw	6
44	s	58
46	m-	9
48	m	13
50	vw	3
52	---	2
54	vw	5
56	vw-	2
58	--	0
62	vw	5
64	w	8
66	w	7
68	vw	3
70	vw	4
72	--	2

with those for La_2O_3 indicate that the atomic coordinates are very similar in the two substances. If the atomic parameters given by Pauling and Shappell[16] for La_2O_3 are correct for Am_2O_3, then each Am atom has three oxygen neighbors at 2.35, one at 2.36 and three at 2.59 Å.

These two structures are commonplace among the sesquioxides of the rare earth elements.[19-21] Ac_2O_3 has the hexagonal structure.[11] Several studies have been made of the temperature dependence of these structures.[19, 21-23] Rapid equilibrium conditions do not prevail, but the data indicate that the hexagonal form is stable at higher temperatures than the cubic form, and that the transition temperature from cubic to hexagonal increases with decreasing cationic radius. Thus, for Nd_2O_3, the cubic form was produced below 775° and the hexagonal form above 850°.[22] Our results with Am_2O_3 are analogous: the cubic form resulted at 600° and the hexagonal form at 800°. This agreement is in accord with the fact that the radii of Am^{+3} and Nd^{+3} are about the same.[12] Since the hexagonal form is unknown for oxides of rare earths smaller

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(19) V. M. Goldschmidt, F. Ulrich, T. Barth, and G. Lunde, "Strukturbericht," Vol. I, pp 261-62.

(20) K. Löhberg, Z. Physik. Chem., <u>B28</u>, 402-7 (1935).

(21) H. Bommer, Z. anorg. u. allgem. Chem., <u>241</u>, 273-80 (1939).

(22) A. Iandelli, Gazz. chim. ital. <u>77</u>, 312-18 (1947).

(23) M. Foex, Compt. rend. <u>224</u>, 1717-19 (1947).

in radius than neodymium, Am_2O_3 is probably near the limit of stability of the hexagonal form. The oxides of elements 96 and above, which have smaller cationic radii, are more likely to occur in the cubic form.

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