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CRYSTAL STRUCTURE AND MELTING POINT  
OF CURIUM METAL

B. B. Cunningham and J. C. Wallmann

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

ABSTRACT

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Curium metal <sup>was</sup> ~~has been~~ found to crystallize in a double  
hexagonal-close-packed structure, similar to that of alpha  
lanthanum. The lattice parameters are:

$$a = 3.496 \pm 0.003\text{\AA} \text{ and}$$

$$c = 11.331 \pm 0.005\text{\AA}.$$

The melting point of the metal was observed to be  
 $1340 \pm 40^\circ\text{C}.$  (auth)

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CRYSTAL STRUCTURE AND MELTING POINT  
OF CURIUM METAL

B. B. Cunningham and J. C. Wallmann

Department of Chemistry and Lawrence Radiation Laboratory  
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Crystal structures of the actinide metals have been reported only through americium.<sup>(1)</sup> The present paper extends the structural data on the metals to curium, the midpoint of the actinide series. The structure and lattice parameters of curium are of interest in connection with proposals which have been made,<sup>(2)</sup> regarding the metallic bonding in the lighter transuranium metals.

EXPERIMENTAL

A. Materials.

Approximately 10 mg of curium, as  $\text{Cm}^{+3}$  was separated from other actinide and rare earth elements by ion exchange.<sup>(3)</sup>

Curium trifluoride was precipitated from the effluent hydrochloric acid solution by the addition of excess aqueous hydrofluoric acid to make the final solution approximately 2M in HF. The precipitation was carried out in a polystyrene centrifuge cone. After centrifuging, the precipitate was washed two times with about

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(1)

D. B. McWhan, B. B. Cunningham and J. C. Wallmann  
J. Inorg. Nucl. Chem. 24, 1025 (1962)

(2)

W. H. Zachariasen, Chapter X, p. 99, in "The Metal Plutonium"  
The University of Chicago Press, 1961.  
A. S. Coffinberry and W. N. Miner, Editors.

(3)

Stanley G. Thompson and M. Luis Muga P/825 USA  
Second International Conference on the Peaceful Uses of Atomic  
Energy. (1958).

40 times its volume of redistilled water and two times with similar amounts of absolute ethyl alcohol. It was then allowed to air-dry by leaving the cone open to the atmosphere. Upon drying, the tri-fluoride compacted into a few small pieces of hard translucent material of porcelain-like appearance. This material presumably is hydrated, since air-dried aqueous precipitates of  $\text{PuF}_3$  have been shown<sup>(4)</sup> to contain chemically bound water.

This material was transferred to a platinum container and placed in a desiccator over phosphorous pentoxide. Consecutive reductions of this material were made after periods of storage ranging from three days to several months.

#### B. Metal Preparation.

Two hundred to five hundred microgram pieces of the tri-fluoride were reduced to metal by reaction with barium metal vapor in a microscale reduction apparatus, consisting essentially of a small double crucible of tantalum, fitted with a plug pierced by a 1/3-1/2 mm effusion hole. This general technique for preparing the actinide metals has been described in detail in an earlier publication.<sup>(1)</sup>

In the case of curium, metal of good appearance was obtained in high yield by maintaining a reduction temperature of from 1315 to 1375°C for two minutes. Additional heating for three minutes at 1235°C served to remove excess barium as well as the barium fluoride slag.

No detectable loss of curium from the crucible system was observed under these conditions; hence the vapor pressure of curium must be much lower than that of americium, since at these temperatures

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(4) J. K. Dawson and R. M. Elliott, The Thermogravimetry of Some Plutonium Compounds, British report A.E.R.E. C/R-1207, June 8, 1953.

samples of americium metal of similar size would have vaporized completely.

Elemental curium prepared as described exhibited a bright silvery surface which did not tarnish readily when exposed to the air.

In attempts to determine the melting point (described below), it was found that molten curium dissolves appreciable amounts of tantalum. Thereafter, the reduction technique was altered, by inserting the piece of trifluoride between two parallel tungsten wires held in a tantalum frame, which was then inserted into the crucible.

#### C. Melting Point Determination.

A technique for determining the melting points of small samples of the lanthanide and actinide metals has been described by McWhan, Cunningham, and Wallmann.<sup>(1)</sup> The only modification required in the case of curium was the substitution of tungsten for tantalum wires. When melting point determinations were attempted using tantalum wire, the melting point of the curium rose gradually with increasing time of contact of the metals at temperatures near the melting point. A similar phenomenon has been reported by Spedding and Daane<sup>(5)</sup> for the rare earth metals.

On substituting tungsten for tantalum the observed melting point appeared to be independent of heating rate, and was found to be  $1340 \pm 40^{\circ}\text{C}$ .

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(5)

F. H. Spedding and A. H. Daane  
Chapter V in Progress in Nuclear Energy, Vol. I, Series V,  
Pergamon Press, New York (1956).



No tungsten was detected by spectrographic emission analysis of samples of curium used for melting point determinations. (See "Analyses and Purity of Materials" below.)

Samples of curium weighing 58, 125, 136  $\mu\text{gm}$  were analyzed separately by spectrographic emission analysis, using copper spark excitation. Limits of detection by this method of analysis for various cationic impurities are given in reference (1). Barium was not detected ( $< 1 \mu\text{gm}$ ) in sample one, nor by special analysis (limit 0.01  $\mu\text{gm}$  of Ba) in sample two. Barium was found to be present at a level of 0.01 atom percent in sample three, which was not analyzed for other cationic impurities. The only cationic impurities detected in the first two samples were 0.1 and 0.2 atom percent of calcium and magnesium respectively in sample one.

#### D. Analyses and Purity of Materials

Analysis of one sample of metal for oxygen, using  $\text{He}^3$  activation<sup>(6)</sup> showed the presence of  $\sim 4000$  ppm.

Mass analysis showed the isotopic composition of the curium used in this work to be:  $\text{Cm}^{244}$ , 96.59%;  $\text{Cm}^{245}$ , 1.59%;  $\text{Cm}^{246}$ , 1.82%.

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(6)

A. Demildt, UCRL-10324 Rev., Jan. 1963

#### E. X-Ray Diffraction.

A few micrograms of metal were loaded into thin-walled quartz capillaries and the diffraction pattern obtained with a Jarrell-Ash Model 80-010 microfocus X-ray unit, using the vertical tube, Y27, and a horizontal line filament cathode, Y37 in conjunction with a Norelco 57 mm radius camera. Similar patterns were obtained from samples taken from three reductions, and from two separately purified batches of curium.

With few exceptions (see "Results and Conclusions" below) all lines could be indexed on the basis of a double hexagonal close packed cell, isostructural with the  $\alpha$  forms of La, Pr, and Nd, and with the double hexagonal form of americium. Reflections from the 10.1, 10.3 and 10.5 planes of the double hexagonal cell distinguished this structure from a simple hexagonal system.

Observed line intensities were compared with calculated values obtained from the 7090 computer, using the intensity program of D. K. Smith. (7)

The diffraction data from one of our samples (297-15A) are given in Table I.

#### RESULTS AND CONCLUSIONS

All lines on film 1675A could be indexed on the basis of a double hexagonal unit cell with  $a = 3.496 \pm 0.003$ ,  $c = 11.331 \pm 0.005$ Å. Satisfactory agreement was obtained between observed and calculated line intensities, as shown in the Table.

The double hexagonal structure was identified in two additional samples of metal prepared by separate reductions of portions of the trifluoride used to make sample 297-15A, and in a third sample

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(7)

D. K. Smith, UCRL-7196, April 8, 1963



prepared from a new batch of  $\text{CmF}_3$  resulting from repurification of the curium. The lattice parameters for all samples were found to be the same as those quoted for sample 297-15A, within the stated limits of error.

One sample of metal showed the presence of three extra lines which could be indexed as fcc with  $a = 5.09\text{\AA}$ , and which may be due to  $\text{CmO}$ . Two additional lines on this film could not be identified with certainty. Metal prepared from repurified curium showed one extra line which was not identified. All lines from the other sample indexed as  $\delta\text{hcp}$ .

Thus, a crystallographic form of metallic curium has been identified and shown to be isostructural with  $\alpha$  La and the  $\delta\text{hcp}$  form of americium. There are four atoms per unit cell, with curium's at: 2 (a) 000,  $00\frac{1}{2}$ , and 2 (c) at  $\frac{1}{3}, \frac{2}{3}, \frac{1}{4}, \frac{2}{3}, \frac{1}{3}, \frac{3}{4}$ . The space group is  $P6_3/\text{mmc} (D_{6h}^{44})$ . The calculated density (for  $\text{Cm}^{244}$ ) is  $13.51 \text{ gms cm}^{-3}$ .

Each curium atom is surrounded by twelve near neighbors—six in the same plane at a distance of  $3.496\text{\AA}$  and three above and three below at  $3.478\text{\AA}$  to give an average radius of  $1.74\text{\AA}$ .

The radius is slightly larger than that for americium ( $1.73\text{\AA}^{(1)}$ ) which suggests a slightly smaller value for the metallic valence for curium.

Zachariasen<sup>(2)</sup> has proposed an empirical relation between metallic radius and metallic valence for the actinide elements which we show in Figure 1 in a form extended to include curium. In constructing his graph Zachariasen assumed that the metallic valence of thorium is 4.0. Other actinide radii-valence correlations were predicted by multiplying the radii of the 3d transition elements by

1.12—the ratio of the radius of thorium to that of zirconium. In the 3d elements the valences are considered to increase monotonically from 1 for rubidium to 10 for palladium. In the actinide metals the valences are assumed equal to the number of 6d plus 7s electrons while 5f electrons are taken to be non-bonding. At constant valence, the actinide contraction in the metals is predicted to be similar to that of the +3 ions.

These assumptions—particularly those regarding metallic valence—are unsupported by other evidence. Zachariasen's graph extrapolates to a metallic valence of 3.8 for curium. In view of the small difference in the metallic radii of americium and curium, we believe it to be equally plausible to assign metallic valence close to 3 for these elements.

Accordingly, we have revised the graph, by vertical displacement, to conform with a +3 valence for curium. New valence assignments are then made for the elements thorium through americium. The revised valence assignments are shown in Figure 1, along with the original assignments of Zachariasen. The new assignment is in good agreement with a +3 valence for actinium and the experimentally measured metallic radius for this element, although such agreement is lacking when the original chart is used.

The revised graph assigns a valence of 3.3 to thorium in the metal.

In support of this proposal we note that the heat of sublimation of thorium, which may be taken as some indication of the strength of metallic bonding, does not represent a reasonable extrapolation of this same property as observed in other group IV metals.

(Heats of sublimation for Ti, Zr, Hf and Th are 112.6, 146.0, 168.0 and 130.0 kcal mol<sup>-1</sup>, respectively.<sup>(8)</sup>)

No doubt much more extensive studies of the properties of the actinide metals need to be made before definite valences can be assigned. We feel that in the meantime, the valence assignments proposed by Zachariasen should be accepted with reservation.

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(8)

Stull and Sinke, Thermodynamic Properties of the Elements, Number 18 in the Advances in Chemistry Series, American Chemical Society, Washington, D. C. (1956).

#### ACKNOWLEDGMENTS

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# THE ACTINIDE METALS ATOMIC RADIUS VS METALLIC VALENCE

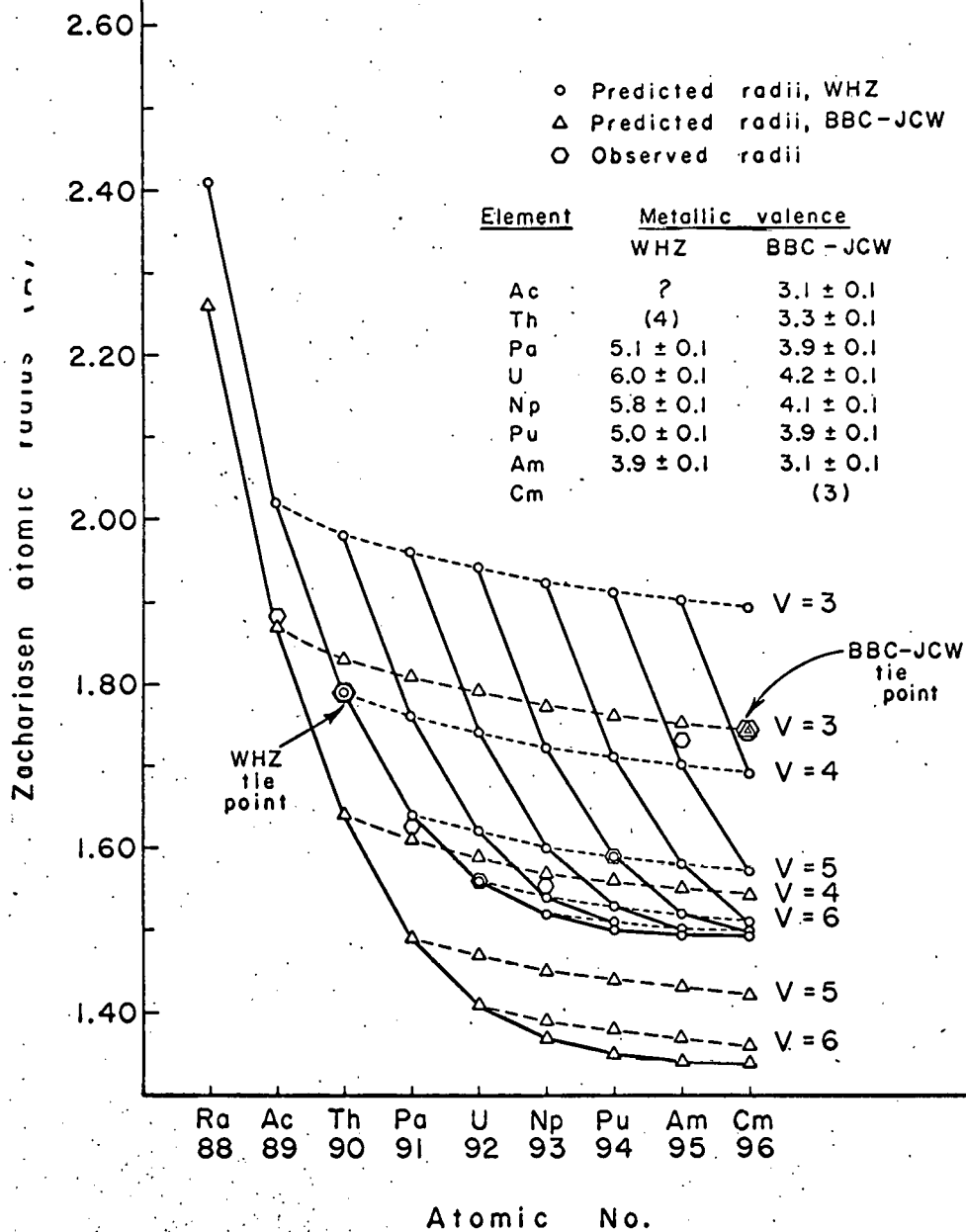


TABLE I. CURIUM METAL ——— DHCP (20°C)

Sample No. 297-15A; Film No. 1675A

 $a = 3.496 \pm 0.003\text{\AA}$ ;  $11.331 \pm 0.005\text{\AA}$ 

hk.l	$\sin^2\theta$ (obs)	$\sin^2\theta$ (calc)	I (obs)	I (calc)
10.0	0.0652	0.0648	T	22
10.1	0.0691	0.0695	M	122
00.4	0.0738	0.0741	S	100
10.2	0.0828	0.0833	S	288
10.3	0.1056	0.1065	W	69
11.0	0.1940	0.1945	M+	75
10.6	0.2309	0.2315	M+	64
11.4	0.2677	0.2685	M	90
20.2	0.2763	0.2778	W+	48
00.8	0.2963	0.2962	W	13
20.6	0.4261	0.4260	W-	25
10.9	0.4386	0.4397	W-	8
21.2	0.4717	0.4723	M-	44
11.8	0.4918	0.4907	M-	37
10.10	0.5260	0.5277	M-	20
30.0	0.5836	0.5835	M-	16
21.6	0.6218	0.6204	M-	36
30.4	0.6573	0.6575	M	32
20.10	0.7214	0.7222	T	19
22.4 $\alpha_1$	0.8490	0.8506	M+	30
11.12 $\alpha_1$	0.8589	0.8596	S	30
31.2 $\alpha_1$		0.8599		
30.8 $\alpha_1$	0.8792	0.8783	M	33
21.10 $\alpha_1$	0.9146	0.9152	M-	44
10.14 $\alpha_1$	0.9708	0.9704	W	40