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	By W. H. Zachariasen
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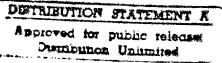
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# LOS ALAMOS SCIENTIFIC LABORATORY of the UNIVERSITY OF CALIFORNIA

Report Written: September 1951

LA-1325

### THE CRYSTAL STRUCTURE OF GAMMA PLUTONIUM

by

W. H. Zachariasen

Work performed under Contract No. W-7405-Eng-36

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#### ABSTRACT

Gamma plutonium is found to be orthorhombic with eight atoms in a unit cell of dimensions (at  $226^{\circ}C$ )  $a_1 = 3.1518$  kX,  $a_2 = 5.7568$  kX,  $a_3 = 10.142$  kX. The calculated density is 17.13. The space group is Fddd and the positions of the eight atoms are: (0 C 0) (0 1/2 1/2) (1/2 0 1/2) (1/2 1/2 0) (1/4 1/4 1/4) (1/4 3/4 3/4) (3/4 1/4 3/4) (3/4 3/4 1/4).

Each plutonium atom is bonded to ten others at an average distance of 3.152 kX, four being at 3.020 kX, two at 3.152 kX and four at 3.285 kX.

The coefficients of thermal expansion are found to be  $\alpha_{100} = -22.5 \times 10^{-6}$ ,  $\alpha_{010} = +47 \times 10^{-6}$ ,  $\alpha_{001} = +94 \times 10^{-6}$ 

#### THE CRYSTAL STRUCTURE OF GAMMA PLUTONIUM

Ву

#### W. H. Zachariasen

The crystal structure is known for only two of the five allotropic forms of plutonium metal. The delta modification is cubic face-centered <sup>1</sup> with a =  $4.63 \text{ A}^{\circ}$  <sup>2</sup> (at  $350^{\circ}$ C), and the epsilon form is cubic body-centered with a =  $3.63 \text{ A}^{\circ}$  <sup>3</sup> (at  $510^{\circ}$ C).

Satisfactory X-ray diffraction patterns of the alpha, beta and gamma forms of plutonium have been available for several years. However, the indexing of these powder patterns has proved to be a very difficult task. The indexing of the pattern of gamma plutonium given in this report succeeded only after a great many hours of intensive work. The patterns of alpha and beta plutonium have not yet been interpreted.

Table 1 gives the observed intensities and sine squares as obtained from a powder diffraction pattern of gamma plutonium taken with  $CuK\alpha$ -radiation at  $226^{\circ}C$ . The  $\alpha_{1}\alpha_{2}$ -doublet is separated for  $\sin^{2}\theta > 0.400$ , and the measurements refer to the stronger component.

The observed sine squares fit the quadratic form

 $\sin^2 \theta = 0.05948 H_1^2 + 0.01728 H_2^2 + 0.005745 H_3^2.$ 

The corresponding orthorhombic unit cell has dimensions  $a_1 = 3.1518 \stackrel{+}{-} 0.0004$ kX,  $a_2 = 5.7568 \stackrel{+}{-} 0.0008$ kX,  $a_3 = 10.142 \stackrel{+}{-} 0.002$  kX. Since the experimentally determined density is 17.0, the unit cell contains eight atoms. The calculated density is  $\rho = 17.13$ .

The translation lattice is face-centered as shown by the fact that reflections are present only from planes for which  $H_1 H_2 H_3$  are either all even or all odd. It is further seen from Table 1 that reflections are missing from planes with  $H_1 H_2 H_3$  all even unless  $\Sigma H_1 = 4n$ .

According to these systematic absences the plutonium atoms are arranged on two interpenetrating face-centered lattices displaced relative to each other by one-fourth of the body diagonal. The positions of the eight atoms in the unit cell are thus:  $(0\ 0\ 0)$   $(0\ 1/2\ 1/2)$ 

- 5 -

TABLE 1. X-RAY DIFFRACTION DATA FOR GAMMA PLUTONIUM (226°C).

00000     0440     062     8       6649     062     8       6769     228     15       6853     139     8       6967     315     8       6967     315     8       7015     313     8       7015     313     8       7015     331     8       7015     331     8       7724     1.1.11     8       7724     1.1.11     8       7724     1.1.11     8       7724     1.1.11     8       7724     1.1.11     8       7724     1.1.11     8       7724     1.1.11     8       8124     2.0.10     8       83346     317     9       83345     335     9       83346     335     9       8487     0666     9       8487     0666     9       9151     1.31     12       9390     17	Int. 13 calc. 142
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8125   8124   2.0.10     8273   8273   0.0.12     8345   8346   317     8345   8346   317     8345   8346   317     8345   8346   317     8392   8394   335     8486   8487   066     8486   8487   066     8800   8798   260     9150   9151   1.3.11     9388   9390   171     9388   9390   171     9517   9517   400     9717   9706   159     9717   9706   159     9717   9705   173     9768   9773   337     9849   9850   173     9867   9868   351	220 21 w-
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	117 17 w
8345   8346   317     8392   8346   315     8392   8394   335     8486   8487   066     8480   8487   066     8800   8798   260     9150   9151   1.3.11     9388   9390   171     9388   9390   171     9517   9517   400     9717   9706   159     9717   9706   159     9717   9705   153     9768   9773   337     9869   9850   173     9867   9868   351	135 16 v
8392   8394   335     8486   8487   066     8480   8487   066     8800   8798   260     9150   9151   1.3.11     9388   9390   171     9388   9390   171     9517   9517   400     9717   9706   159     9717   9706   159     9768   9773   337     9869   9850   173     9867   9868   351	008 · 8
8486   8487   066     8800   8798   260     9150   9151   1.3.11     9180   8798   250     9170   9707   171     9717   9706   159     9717   9706   159     9717   9707   159     9717   9706   159     9717   264   173     9768   9773   337     9849   9850   173     9867   9868   351	044 15 1
8800   8798   260     9150   9151   1.3.11     9188   9390   171     9388   9390   171     9517   9517   400     9717   9706   159     9717   9706   159     9717   264   9717     9749   9850   173     9849   9850   173     9867   9868   351	224 30 v
9150   9151   1.3.11     9388   9390   171     9517   9517   400     9517   9517   264     9717   9706   159     9717   9706   159     9717   9706   159     9717   9706   159     9718   9717   264     9769   9773   337     9849   9850   173     9867   9868   351	206 12 w
9388   9390   171     9517   9517   9517   400     9717   9706   159     9717   9717   264     9717   9717   264     9717   9717   264     9717   9717   264     9717   9768   9713   337     +   9849   9850   173     +   9867   9868   351	137 9 w
9517 9517 400 9717 9706 159 9717 264 9768 9773 337 9849 9850 173 9867 9868 351	151 9 w
9717 9706 159   9717 264   9768 9773 337   9849 9850 173   9867 9868 351	115 9 <sup>w</sup>
9768 9773 337 9849 9850 173 9867 9868 351	242 18 r
9708 9713 551 9849 9850 173 9867 9868 351	153 9
9849 9850 173 9867 9868 351	311 9 <sup>1</sup>
9867 9868 351	313 8
	0.2.10 8

- 6 -

 $(1/2 \ 0 \ 1/2) (1/2 \ 1/2 \ 0) (1/4 \ 1/4 \ 1/4) (3/4 \ 3/4 \ 1/4) (3/4 \ 1/4 \ 3/4) (1/4 \ 3/4 \ 3/4).$  This atomic configuration corresponds to the space group symmetry Fddd  $(D_{2h}^{24})$  with the eight plutonium atoms structurally equivalent. A perspective drawing of one unit cell is shown in Figure 1.

The last column of Table 1 gives the intensities calculated from the formula

$$\mathbf{I} \alpha | \mathbf{F} |^2 \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}$$

The absorption and temperature factors have not been taken into account. Observed and calculated intensities should accordingly be compared only for neighboring reflections.

The crystal structure of gamma plutonium is unlike that of any other metal. Each plutonium atom is bonded to ten others at approximately the same distance, as illustrated in Figure 2. The individual interatomic distances are (at  $226^{\circ}C$ ): Pu - 4Pu = 3.020 kX, Pu - 2Pu = 3.152 kX, Pu - 4Pu = 3.285 kX. The average distance of Pu - 10Pu = 3.16A compares to Pu - 12Pu =  $3.27A^{\circ}$  in delta plutonium and Pu - 8Pu = 3.15A in epsilon plutonium.

When allowance is made for the effect of coordination number one finds a metallic radius of 1.60Å for plutonium in the gamma form as compared to the radius 1.63Å in delta plutonium. The difference in radius for the two forms is possibly due to the fact that the transition from the delta to the gamma form is accompanied by the promotion of a fraction of an electron from the 5f to the 6d level. From the value of 1.60Å for the radius of plutonium in the gamma form, one would estimate that there are about three electrons in the 5f shell.

Normal to the  $a_3$ -axis there are pseudo-hexagonal layers, the  $a_3$ -period corresponding to four times the layer separation. The bond lengths within a layer are 3.152 kX and 3.285 kX. The bond length between layers is 3.020 kX.

Table 2 shows the variation of the unit cell dimensions with temperature in the range  $161^{\circ} - 265^{\circ}C$ , and Table 3 gives the deduced values of the three principal coefficients of thermal expansion.

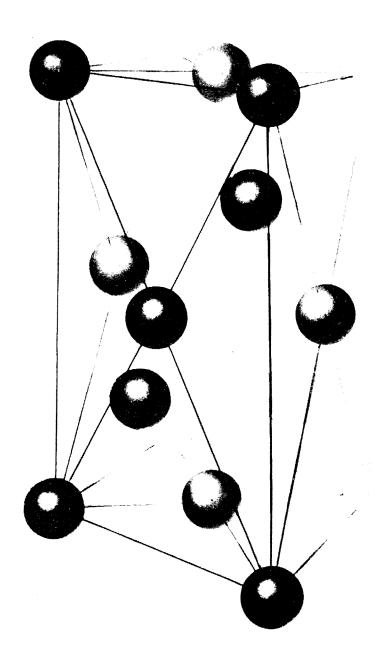


Fig. 1. The Unit Cell of Gamma Plutonium.

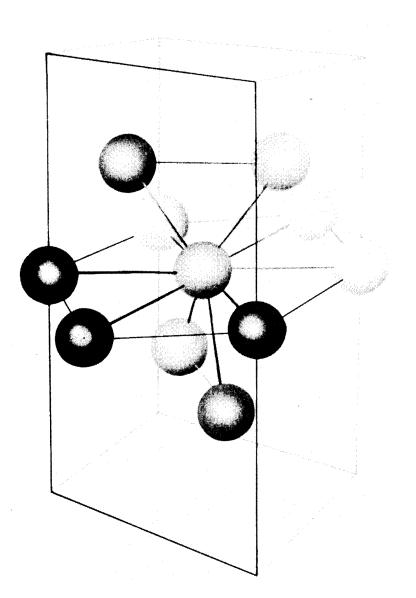


Fig. 2. A portion of the unit cell illustrating the tenfold coordination. Relative to Figure 1, the origin of the unit cell has been displaced by  $(0\ 0\ 1/2)$ .

	TABLE 2.	UNIT CELL D	IMENSIONS (II	N <b>kX</b> )	
	AND	CALCULATED	DENSITY AT		
VARIOUS TEMPERATURES					
	161 <sup>0</sup>	200 <sup>0</sup>	226 <sup>0</sup>	265 <sup>0</sup>	Accuracy
a	3.1568	3.1527	3.1518	3.1490	<sup>+</sup> 0.0004 kX
a <sub>2</sub>	5.7400	5.7475	5.7568	5.7670	<del>+</del> 0.0008
a <sub>3</sub>	10.083	10.111	10. 14 <b>2</b>	10.180	+0.002
ρ	17.26	17.21	17.13	17.06	

TABLE 3.	COEFFICIENTS	OF	THERMAL	EXPANSION
$10^{6} \alpha_{100}$				- 22.5 <sup>+</sup> 1.0
$10^{6} \alpha_{010}$				+ 47 - 2
$10^{6} \alpha_{001}$				+ 94 <sup>+</sup> 4

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#### REFERENCES

<sup>1</sup> R. C. L. Mooney and W. H. Zachariasen, CK-1367, CK-1377, CK-1968 and CN-2069.

<sup>2</sup> F. J. Schnettler and E. R. Jette, LAMS-211, p. 21. F. H. Ellinger of Los Alamos Scientific Laboratory has obtained evidence that  $4.624 \stackrel{+}{=} 0.001$  kX is a somewhat better value for the unit cell edge of delta plutonium at  $350^{\circ}$ C. However, there is good reason to suspect that the specific volume of the delta phase at any given temperature is strongly dependent on previous history, and it is not clear that "equilibrium" values of unit cell dimensions have ever been determined.

<sup>3</sup> F. J. Schnettler and E. R. Jette, LAMS-249, p. 17.

#### ACKNOWLEDGEMENT

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The author is also indebted to Eric R. Jette, CMR Division, and to A. S. Coffinberry, Group CMR-5, for having provided the opportunity for this investigation to be carried out.