Acta Cryst. (1955). **8**, 431

Crystal Chemical Studies of the 5*f*-Series of Elements. XXIV. The Crystal Structure and Thermal Expansion of γ-Plutonium*

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(*Received* 10 *February* 1955)

γ-Plutonium is found to be orthorhombic with eight atoms in a unit cell of dimensions (at 235° C.) $a_1 = 3\cdot1587\pm0\cdot0004$, $a_2 = 5\cdot7682\pm0\cdot0004$, $a_3 = 10\cdot162\pm0\cdot002$ Å. The calculated density is $17\cdot14\pm0\cdot01$ g.cm.$^{-3}$. The space group is *Fddd* and the positions of the eight atoms are: (0, 0, 0), $(0, \frac{1}{2}, \frac{1}{2})$, $(\frac{1}{2}, 0, \frac{1}{2})$, $(\frac{1}{2}, \frac{1}{2}, 0)$, $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, $(\frac{1}{4}, \frac{3}{4}, \frac{3}{4})$, $(\frac{3}{4}, \frac{1}{4}, \frac{3}{4})$, $(\frac{3}{4}, \frac{3}{4}, \frac{1}{4})$.

Each plutonium atom is bonded to ten others at an average distance of 3·157 Å, four being at 3·026 Å, two at 3·159 Å and four at 3·288 Å.

The mean linear coefficients of thermal expansion are found to be $10^6\alpha_{[100]} = -19\cdot7\pm1\cdot0$/°C., $10^6\alpha_{[010]} = 39\cdot5\pm0\cdot6$/°C., $10^6\alpha_{[001]} = 84\cdot3\pm1\cdot6$/°C.

Crystal structure

The crystal structure is known for four of the six allotropic forms of plutonium metal.† The γ form (Zachariasen, 1952), reported herein, is orthorhombic face-centered, δ is cubic face-centered (Mooney & Zachariasen, 1944) with $a = 4\cdot636\pm0\cdot001$ Å at 350° C. (Jette, 1955; Schnettler & Jette, 1945*a*), δ' is tetragonal body-centered (Jette, 1955) with $a_1 = 3\cdot33\pm0\cdot01$ Å, $a_3 = 4\cdot46\pm0\cdot01$ Å at 470° C., and ε is cubic body-centered with $a = 3\cdot639\pm0\cdot001$ Å at 510° C. (Jette, 1955; Schnettler & Jette, 1945*b*).

Satisfactory X-ray diffraction patterns of the α, β and γ 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 γ plutonium given in this report succeeded only after a great many hours of intensive work. The patterns of α and β plutonium have not yet been interpreted.

Table 1 gives the observed intensities and sine squares as obtained from a powder diffraction pattern of γ plutonium (purity 99·85%) taken with Cu $K\alpha$ radiation in a Unicam high-temperature camera at 235° C. The $\alpha_1\alpha_2$ doublet is separated for $\sin^2\theta > 0\cdot400$, and the measurements refer to the stronger component.

The observed sine squares fit the quadratic form

$$\sin^2\theta = 0\cdot05948H_1^2+0\cdot01728H_2^2+0\cdot005745H_3^2\,.$$

The corresponding orthorhombic unit cell has dimensions

$$a_1 = 3\cdot1587\pm0\cdot0004,\ a_2 = 5\cdot7682\pm0\cdot0004,\ a_3 = 10\cdot162\pm0\cdot002 \text{ Å}\,.$$

Since the experimentally determined density is 17·0 g.cm.$^{-3}$, the unit cell contains eight atoms. The calculated density is $\varrho = 17\cdot13$ g.cm.$^{-3}$.

The translation lattice is face-centered as shown by the fact that reflections are present only from planes for which $H_1H_2H_3$ are either all even or all odd. It is further seen from Table 1 that reflections are missing from planes with $H_1H_2H_3$ all even unless $\Sigma H_j = 4n$.

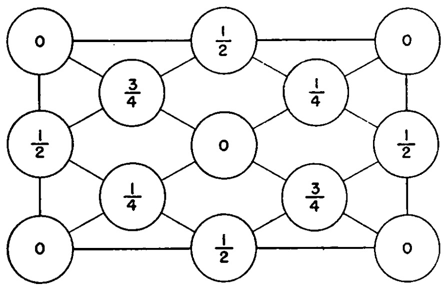

Fig. 1. The atomic positions in the unit cell of γ plutonium projected on a (001) face.

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), $(0, \frac{1}{2}, \frac{1}{2})$, $(\frac{1}{2}, 0, \frac{1}{2})$, $(\frac{1}{2}, \frac{1}{2}, 0)$, $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, $(\frac{3}{4}, \frac{3}{4}, \frac{1}{4})$, $(\frac{3}{4}, \frac{1}{4}, \frac{3}{4})$, $(\frac{1}{4}, \frac{3}{4}, \frac{3}{4})$. This atomic configuration corresponds to the space group symmetry *Fddd* (D_{2h}^{24}) with the eight plutonium atoms structurally equivalent. A projection of one unit cell on the *c*-face is shown in Fig. 1.

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* Work done under the auspices of the Atomic Energy Commission.

† A new allotropic form of plutonium, designated δ', was discovered in the past year (Lord, 1954; Smith, 1954; Jette, 1955).

Table 1. *X-ray diffraction data for γ plutonium at 235° C.*

I_o	$(\sin^2\theta)_o$	$(\sin^2\theta)_c$	$H_1H_2H_3$	I_c
s	0·0836	0·0830	111	142
w	0·0925	0·0919	004	61
m+	0·0949	0·0943	022	115
m	0·1297	0·1290	113	80
m−	0·2218	0·2209	115	36
w+	0·2265	0·2257	131	36
w+	0·2616	0·2609	202	28
w+	0·2723	0·2717	133	26
w+	0·2788	0·2781	026	25
vw	0·2860	0·2853	040	12
w+	0·3100	0·3092	220	21
w	0·3590	0·3588	117	17
w	0·3637	0·3636	135	16
vw	0·3687	0·3677	008	8
w+	0·3772	0·3772	044	15
m	0·4012	0·4011	224	30
w	0·4448	0·4447	206	12
w−	0·5017	0·5015	137	9
w−	0·5111	0·5110	151	9
vw	0·5427	0·5426	119	9
*m**	0·5461	0·5462	242	18
vw	0·5574	0·5570	153	9
*w**	0·5597	0·5588	311	9
vw+	0·6046	0·6048	313	8
vw+	0·6458	0·6458	0,2,10	8
w−*	0·6490	0·6489	155	8
*w**	0·6526	0·6530	048	8
w−	0·6648	0·6649	062	8
w+	0·6766	0·6769	228	15
vw+	0·6853	0·6853	139	8
vw+	0·6970	0·6967	315	8
*w**	0·7011	0·7015	331	8
m−	0·7300	0·7300	246	15
w−	0·7473	0·7475	333	8
vw	0·7724	0·7724	1,1,11	8
w−	0·7870	0·7868	157	8
w−	0·8125	0·8124	2,0,10	8
vw−	0·8273	0·8273	0,0,12	4
w−	0·8345	0·8346	317	9
w+*	0·8392	0·8394	335	9
w	0·8486	0·8487	066	9
w	0·8800	0·8798	260	10
w−	0·9150	0·9151	1,3,11	12
w	0·9388	0·9390	171	13
vw	0·9517	0·9517	400	8
ms	0·9717	{ 0·9706	159	19
		{ 0·9717	264	38
*m**	0·9768	0·9773	337	21
w+	0·9849	0·9850	173	27
w+	0·9867	0·9868	351	29

* Coincidence with α_2 line.

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

$$I \propto |F^2| \frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta} p\,.$$

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 γ plutonium is unlike that of any other metal. Each plutonium atom is bonded to ten others at approximately the same distance, as illustrated in Fig. 2. The individual interatomic distances are (at 235° C.): Pu−4Pu=3·026 Å, Pu−2Pu=3·159 Å, Pu−4Pu=3·288 Å. The average distance of Pu−10Pu=3·16 Å compares to Pu−12Pu=3·27 Å in δ plutonium and Pu−8Pu=3·15 Å in ε plutonium.

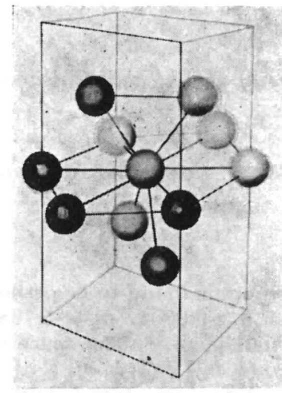

Fig. 2. A portion of the unit cell illustrating the tenfold coordination. Relative to Fig. 1, the origin of the unit cell has been displaced by (0, 0, ½).

When allowance is made for the effect of coordination number one finds a metallic radius of 1·60 Å for plutonium in the γ form as compared to the radius 1·63 Å in δ plutonium. The difference in radius for the two forms is possibly due to the fact that the transition from the δ to the γ form is accompanied by the promotion of a fraction of an electron from the 5*f* to the 6*d* level. From the value of 1·60 Å for the radius of plutonium in the γ form, one would estimate that there are about three electrons in the 5*f* 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 3·159 Å and 3·288 Å. The bond length between layers is 3·026 Å.

Thermal expansion

The thermal expansion of γ plutonium was determined from a series of X-ray diffraction powder patterns taken in a Unicam high-temperature camera in the range 213–312° C., using Cu *Kα* radiation. The powder sample, contained in an evacuated clear silica capillary, was prepared from plutonium metal filings of 99·97 % purity mixed with a small proportion of pure silver powder to serve for temperature measurement. The lattice constant of the silver at each temperature was determined by graphical extrapolation of the high-angle lines using the Nelson & Riley (1945) function, and the corresponding temperature was taken from the thermal expansion data of Hume-Rothery & Reynolds (1938). The uncertainty in each measurement of the silver lattice constant was less than ±0·0002 Å, which corresponds to an uncertainty in each temperature measurement of about ±2° C. The lattice constants of the γ plutonium were evaluated by Cohen's (1935, 1936) analytical extrapolation method with the aid of IBM machines.

The lattice constant versus temperature data are listed in Table 2 and plotted in Fig. 3. It is seen that

Table 2. *Lattice constants as function of temperature*

Temperature (±2° C.)	a_1 (Å)	a_2 (Å)	a_3 (Å)
213	3·16052	5·76275	10·1442
230	3·15889	5·76674	10·1557
233	3·15909	5·76769	10·1615
238	3·15908	5·76766	10·1610
239	3·15853	5·76925	10·1684
242	3·15847	5·77006	10·1706
243	3·15797	5·77041	10·1691
246	3·15842	5·77083	10·1726
258	3·15622	5·77371	10·1834
264	3·15642	5·77521	10·1880
272	3·15645	5·77648	10·1941
289	3·15505	5·78015	10·2060
292	3·15538	5·78062	10·2101
296	3·15554	5·78084	10·2088
304	3·15492	5·78388	10·2240
307	3·15432	5·78459	10·2243
309	3·15410	5·78532	10·2282
312	3·15397	5·78574	10·2290

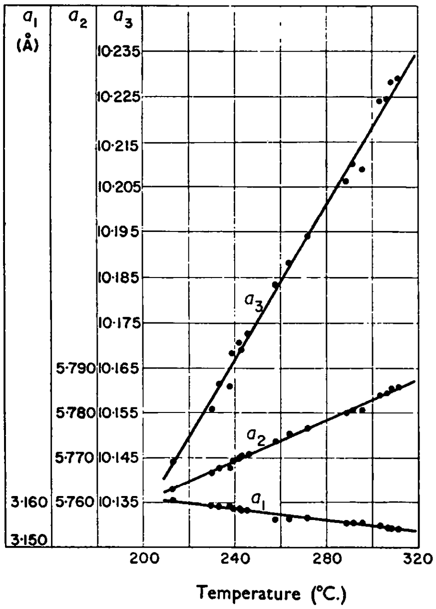

Fig. 3. Lattice constants of γ plutonium versus temperature.

straight lines represent the expansion quite well. Accordingly, the data were fitted to straight lines by the least-squares method yielding the following equations:

$$a_1 = (3{\cdot}16095 \pm 0{\cdot}00023) - (6{\cdot}22 \pm 0{\cdot}32)10^{-5}(t-200)\,,$$
$$a_2 = (5{\cdot}76011 \pm 0{\cdot}00023) + (22{\cdot}75 \pm 0{\cdot}32)10^{-5}(t-200)\,,$$
$$a_3 = (10{\cdot}1325 \pm 0{\cdot}0012) + (85{\cdot}4 \pm 1{\cdot}6)10^{-5}(t-200)\,,$$

where t is in °C. and the precision measures are standard deviations.

The true linear coefficient of expansion is expressed by $\alpha = (1/a)(da/dt)$. The derivative da/dt is the slope of the line which divided by the lattice constant at each temperature gives the true or instantaneous coefficient at that temperature. The values of true α are listed in Table 3, where the standard deviations

Table 3. *Thermal expansion coefficients*

Temperature (°C.)	True $\alpha \times 10^{-6}$/°C. [100]	[010]	[001]
210	−19·68	39·48	84·21
260	−19·70	39·40	83·86
310	−19·72	39·32	83·51

in the [100], [010] and [001] crystallographic directions are 5·1, 1·4 and 1·9% respectively.

The mean linear coefficients for each direction computed for the range 210–310° C. are:

$$10^6\bar{\alpha}_{[100]} = -19{\cdot}7 \pm 1{\cdot}0/°\text{C.}\,,$$
$$10^6\bar{\alpha}_{[010]} = 39{\cdot}5 \pm 0{\cdot}6/°\text{C.}\,,$$
$$10^6\bar{\alpha}_{[001]} = 84{\cdot}3 \pm 1{\cdot}6/°\text{C.}$$

For polycrystalline γ plutonium, free from preferred orientation, the mean linear coefficient, expressed by

$$\bar{\alpha} = \tfrac{1}{3}(\bar{\alpha}_{[100]} + \bar{\alpha}_{[010]} + \bar{\alpha}_{[001]}),\ \text{is}\ (34{\cdot}7 \pm 0{\cdot}7) \times 10^{-6}/°\text{C.}$$

The mean volume coefficient, expressed by $\bar{\alpha}_v = 3\bar{\alpha}$, is $(104 \pm 2) \times 10^{-6}$/°C.

The authors wish to thank Dr Max Goldstein for the IBM calculations and Miss Marian Gibbs for measuring the films.

One of us (W. H. Z.) is also indebted to Drs E. R. Jette and A. S. Coffinberry for having provided the opportunity for the crystal-structure investigation to be carried out.

References

Cohen, M. U. (1935). *Rev. Sci. Instrum.* **6**, 68.
Cohen, M. U. (1936). *Rev. Sci. Instrum.* **7**, 155.
Hume-Rothery, W. & Reynolds, P. W. (1938). *Proc. Roy. Soc.* A, **167**, 25.
Jette, E. R. (1955). *J. Chem. Phys.* In the Press.
Lord, W. B. H. (1954). *Nature, Lond.* **173**, 535.
Mooney, R. C. L. & Zachariasen, W. H. (1944). Metallurgical Project Reports, CK-1367, CK-1377, CK-1968 and CN-2069.
Nelson, J. B. & Riley, D. P. (1945). *Proc. Phys. Soc.* **57**, 160.
Schnettler, F. J. & Jette, E. R. (1945*a*). LAMS-211.
Schnettler, F. J. & Jette, E. R. (1945*b*). LAMS-249.
Smith, C. S. (1954). *Metal Progr.* **65**, 81.
Zachariasen, W. H. (1952). LA-1325.