angles different by only 1·4° on the average from those reported in Table 4. However, these additional intensities were not as reliable as those in Table 1, and hence the detailed results have not been revised. Finally, values of F_c for the 548 reflections which are 'unobserved' but which are in the range covered by the photographs were all less (usually much less) than twice the observational limit, but these absent reflections were not included in the least squares refinements.

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The Crystal Structure of Beta Plutonium Metal[*]

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β–Pu is monoclinic body-centered with 34 atoms per unit cell. At 190 °C

$$a=9{\cdot}284,\ b=10{\cdot}463,\ c=7{\cdot}859\ \text{Å},\ \beta=92{\cdot}13^\circ$$

and the density is 17·70 g.cm.$^{-3}$.

The space group is $I2/m$. One set of two plutonium atoms are in centers of symmetry. Three sets of four plutonium atoms are in reflection planes, one set of four on twofold axes and two sets of eight in general positions. The thirteen parameters in the structure have been determined to an accuracy of about 0·04 Å.

The seven different kinds of plutonium atoms in the structure have coordination number of twelve, thirteen or fourteen. The mean atomic radius is 1·60 Å for coordination number twelve.

Introduction

Plutonium metal can be prepared in six allotropic forms. The various transition temperatures on heating have been reported as follows (Jette, 1955)

Transformation	Temperature	Transformation	Temperature
$\alpha \to \beta$	122 ± 2 °C.	$\delta \to \delta'$	451 ± 4 °C.
$\beta \to \gamma$	206 ± 3	$\delta' \to \varepsilon$	476 ± 5
$\gamma \to \delta$	319 ± 5	$\varepsilon \to$ liq.	640 ± 2

Complete crystal structures are known for all but the β-form. α-Plutonium is monoclinic with 16 atoms to the unit cell, eight different kinds of atoms and 16 degrees of freedom (Zachariasen & Ellinger, 1957). The γ-phase is orthorhombic face-centered with eight equivalent atoms per unit cell and there are no position parameters (Zachariasen & Ellinger, 1955). The three high temperature forms have simple structures: δ-plutonium is cubic face-centered, ε-plutonium cubic body-centered, while δ'-plutonium is tetragonal body-centered (Ellinger, 1956).

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As reported earlier β-plutonium is monoclinic body-centered with 34 atoms per unit cell (Zachariasen & Ellinger, 1959). In this paper an account is given of the complete structure determination of this phase.

The experimental data

Both the α–β and β–γ transitions (in particular the former) are sluggish, and small impurity additions may affect appreciably the transition temperatures. Thus, X-ray diffraction patterns of the same sample of pure plutonium were obtained at both 93 and at 190 °C., and of a sample of plutonium with 2% uranium added at 83, 139, 186 and 252 °C. Indeed, using a preparation containing a small, but unknown, amount of zirconium the β-phase diffraction pattern was obtained at room temperature.

All attempts to prepare single crystals of beta plutonium large enough for X-ray diffraction studies have failed. Accordingly, the structure determination had to be deduced entirely from 'powder' diffraction patterns.

The indexing of the diffraction pattern as well as the determination of the structure was based upon experimental data obtained with a General Electric diffractometer which had been adapted for high temperature work. In these experiments the sample was a flat slab of metal with electro-polished surface, and Cu $K\alpha$ radiation was usually employed. Powder photographs prepared with metal filings were used to determine whether or not there was appreciable preferential orientation in the large samples utilized in the diffractometer experiments. Considerable orientation effects were observed frequently, and so were small amounts of oxide impurity (PuO, Pu_2O_3–Pu_4O_7, PuO_2).

The intensity data used in the structure determination were obtained with a preparation containing 2% of uranium. The uranium addition has a small effect on the unit cell dimensions (causing a decrease of about 0·05% as compared with pure plutonium) and none on intensities. This particular sample was selected because it was practically free of oxide contamination and preferred orientation, and because excellent diffractometer traces with Cu $K\alpha$-radiation were obtained at temperatures ranging from 83 to 252 °C.

The intensities were measured by planimetering the area under the diffraction peaks. Diffraction maxima of comparable intensity could be resolved as distinct peaks if their sine square values differed by more than 10×10^{-4}. For diffractometer experiments the intensity expression was taken to be

$$I \propto p|F|^2 \exp\left[-2M\right](1+\cos^2 2\theta)/\sin^2\theta\cos\theta \quad (1)$$

where p is the multiplicity for the reflecting plane and where the other symbols have their usual meanings.

Unit-cell dimensions

The first major task of the investigation was the indexing of the diffraction pattern.

All attempts to interpret the diffraction pattern on the basis of orthorhombic or higher symmetry having failed, it was assumed as a working hypothesis that beta plutonium might be monoclinic.

A method to interpret powder diffraction patterns of monoclinic crystals was developed for the purpose of solving the alpha plutonium structure. This procedure was applied and led to success also for the beta modification. The method (which will be described in a separate article) is trivially simple and requires only hand computations.

Unit cell dimensions have been determined for a number of beta plutonium preparations, and some of the results are given in Table 1. In Table 2 are listed approximate values for the linear coefficients of thermal expansion. The coefficient α_2 refers to the b-axis, and φ is the angle between the direction of maximum expansion (α_1) and the a-axis measured in the obtuse angle β.

The pronounced anisotropy in the thermal expansion proved useful. Many diffraction lines which are superimposed in the pattern at one temperature can be resolved into individual components when the temperature is changed sufficiently.

This is illustrated in Fig. 1 which gives a small section of the diffraction patterns of the 98 Pu–2 U sample at 83, 139, 186 and 252 °C.

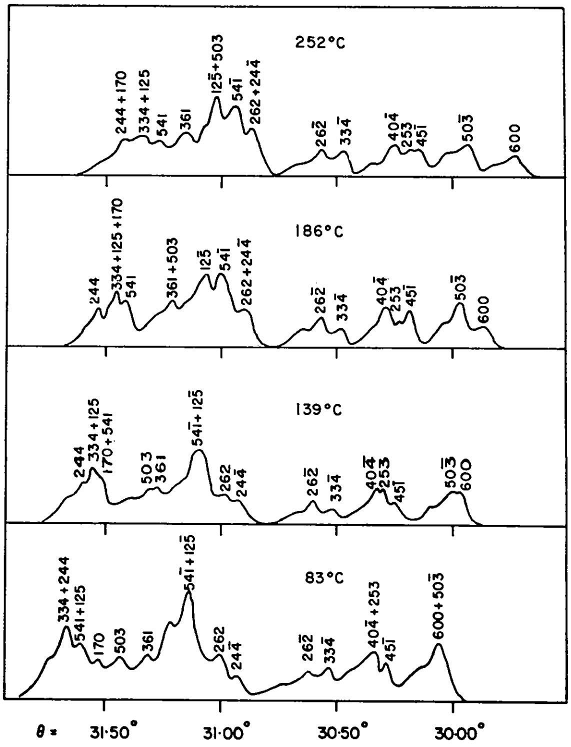

Fig. 1. Illustrates changes in the diffraction pattern due to the anisotropic thermal expansion.

Table 1. *Unit cell dimensions**

Sample	Temperature	*a* (Å)	*b* (Å)	*c* (Å)	*β* (°)
Pure Pu	93 °C.	9·227	10·449	7·824	92·54
Pure Pu	190	9·284	10·463	7·859	92·13
99 Pu–1 Ce	133	9·251	10·436	7·834	92·35
99 Pu–1 Ce	172	9·260	10·449	7·846	92·24
99 Pu–1 Ce	202	9·286	10·451	7·852	92·06
98 Pu–2 U	83	9·215	10·418	7·815	92·52
98 Pu–2 U	139	9·242	10·433	7·824	92·36
98 Pu–2 U	186	9·264	10·439	7·841	92·22
98 Pu–2 U	252	9·302	10·444	7·859	91·97

* Calculated density for pure Pu is 17·70 g.cm.$^{-3}$ at 190 °C. Precision is ±0·002 Å for *a*, *b*, *c*, and ±0·02° for *β*.

Table 2. *Principal linear coefficients of thermal expansion* (×10^6)

	α_1	α_2	α_3	$\bar{\alpha}$	φ
Pure Pu	94	14	19	42	40°
99 Pu–1 Ce	84	21	7	37	38°
98 Pu–2 U	79	13	15	38	35°

Table 3. *Observed reflections*

HKL	83 °C. sin² θ Obs.	83 °C. sin² θ Calc.	Intensity obs.	252 °C. sin² θ Calc.	252 °C. sin² θ Obs.
$20\bar{2}$*	0·0641	0·0640	15	0·0637	0·0639
310*	0·0685	0·0685	11	0·0672	0·0673
202*	0·0699	0·0698	28	0·0682	0·0683
$23\bar{1}$	0·0861	0·0855	318	0·0849	0·0857
$22\bar{2}$		0·0859		0·0855	
040*	0·0874	0·0875	66	0·0870	0·0873
231*	0·0883	0·0884	121	0·0872	
222*	0·0925	0·0917	67	0·0900	0·0902
$32\bar{1}$		0·0924	200	0·0915	0·0923
$10\bar{3}$		0·0924		0·0917	
013		0·0931		0·0920	
$1\bar{3}2$*		0·0937	82	0·0931	0·0932
321	0·0969	0·0968	442	0·0949	0·0952
103		0·0968		0·0951	
132		0·0966		0·0954	
$31\bar{2}$	0·1034	0·1030	82	0·1023	0·1030
$14\bar{1}$		0·1035		0·1030	
141*	0·1049	0·1049	43	0·1041	0·1042
312*	0·1122	0·1118	14	0·1090	0·1089
400*		0·1120	29	0·1098	0·1098
330*		0·1122	30	0·1107	0·1110
$12\bar{3}$*	0·1145	0·1143	7	0·1135	0·1135
240*	0·1157	0·1155	11	0·1145	0·1145
$21\bar{3}$*	0·1171	0·1167	21	0·1161	0·1163
123*	0·1188	0·1186	21	0·1168	0·1170
$41\bar{1}$*	0·1245	0·1243	51	0·1226	0·1229
042*	0·1266	0·1264	45	0·1255	0·1258
411*	0·1301	0·1301	5	0·1271	0·1270
033*	0·1371	0·1368	7	0·1355	0·1358
150	0·1440	0·1437	11	0·1428	0·1429
$30\bar{3}$		0·1441		0·1433	
$40\bar{2}$	0·1453	0·1451	5	0·1438	0·1441
$24\bar{2}$*	0·1520	0·1514	4	0·1508	0·1508
332	0·1552	0·1555	6	0·1526	0·1532
004		0·1557		0·1539	
402	0·1570	0·1567	24	0·1528	
303		0·1571		0·1534	
$23\bar{3}$*	0·1608	0·1604	3	0·1597	0·1598
$11\bar{4}$*	0·1657	0·1653	6	0·1639	0·1643
$43\bar{1}$*	0·1682	0·1680	6	0·1661	0·1662
233*	0·1693	0·1692	14	0·1663	
422	0·1785	0·1786	10	0·1745	0·1745
323		0·1790		0·1751	
024		0·1776	6	0·1756	0·1755
$20\bar{4}$		0·1779	5	0·1769	0·1767
$50\bar{1}$*	0·1810	0·1811	11	0·1784	0·1785
152	0·1845	0·1840	20	0·1824	0·1828
143		0·1842		0·1821	
060*	0·1967	0·1968	9	0·1958	0·1962
$22\bar{4}$*	0·1999	0·1998	10	0·1987	0·1990
521*	0·2102	0·2102	9	0·2057	0·2057
224	0·2112	0·2114	4	0·2075	0·2073
$16\bar{1}$*	0·2125	0·2128	7	0·2117	0·2119
161*	0·2141	0·2142	11	0·2128	0·2131
134		0·2148		0·2119	
$31\bar{4}$*	0·2157	0·2155	11	0·2144	0·2147
053	0·2243	0·2243	19	0·2225	0·2229
260		0·2248		0·2233	
512*	0·2265	0·2267	10	0·2211	0·2214
062*	0·2357	0·2357	7	0·2343	0·2344
044*	0·2434	0·2432	25	0·2409	0·2414
600*	0·2520	0·2520	26	0·2471	0·2470
$50\bar{3}$*		0·2517	29	0·2498	0·2501
$45\bar{1}$*	0·2555	0·2555	18	0·2531	0·2532
$53\bar{2}$	0·2562	0·2560	14	0·2534	
253*		0·2566		0·2534	
$40\bar{4}$*		0·2561	20	0·2547	0·2549
433		0·2575	12	0·2520	0·2516
$33\bar{4}$*	0·2593	0·2592	20	0·2579	0·2582
$61\bar{1}$	0·2627	0·2629	8	0·2588	
$26\bar{2}$*	0·2607	0·2608	17	0·2595	0·2597
$24\bar{4}$*	0·2654	0·2654	20	0·2639	0·2643
262*	0·2667	0·2666	29	0·2640	
$54\bar{1}$*	0·2686	0·2686	45	0·2654	0·2654
$12\bar{5}$*		0·2686	45	0·2667	0·2667
503*	0·2733	0·2735	24	0·2665	
361*	0·2714	0·2717	32	0·2689	0·2689
170*	0·2748	0·2748	16	0·2734	0·2730
244*	0·2768	0·2770	15	0·2729	
334*		0·2767	27	0·2713	0·2718
125*	0·2758	0·2758	12	0·2718	
541*		0·2758	13	0·2710	0·2708
215*	0·2840	0·2841	14	0·2790	0·2789
$16\bar{3}$*	0·2892	0·2892	7	0·2875	0·2877
424*	0·3011	0·3012	9	0·2943	0·2944
$62\bar{2}$*	0·3038	0·3041	8	0·3007	0·3006
$17\bar{2}$*	0·3126	0·3123	7	0·3107	0·3106
325*	0·3391	0·3391	15	0·3324	0·3334
640		0·3395		0·3342	
$44\bar{4}$*	0·3438	0·3436	42	0·3417	0·3418
710	0·3486	0·3485	8	0·3418	
514*	0·3510	0·3507	5	0·3420	
080*	0·3497	0·3498	8	0·3481	0·3482
552*	0·3579	0·3579	11	0·3516	0·3517
444*	0·3667	0·3668	8	0·3596	0·3598
$37\bar{2}$*	0·3655	0·3654	14	0·3634	0·3636
$64\bar{2}$*	0·3696	0·3697	14	0·3659	0·3656
372*	0·3740	0·3741	9	0·3701	0·3701
$27\bar{3}$*	0·3795	0·3791	6	0·3772	0·3765
642*	0·3872	0·3871	26	0·3793	0·3791
206		0·3871		0·3804	
471*	0·3921	0·3925	13	0·3881	0·3877
$72\bar{3}$*	0·4372	0·4372	18	0·4329	0·4324
046		0·4379		0·4332	

* Uniquely indexed reflections.

The X-ray diffraction patterns have been completely indexed up to $\sin^2\theta = 0{\cdot}400$ for Cu $K\alpha$ radiation.

Symmetry permits 240 different reflections in this angular range, but only about one hundred can be observed, and some of these cannot be uniquely indexed. The measurable diffraction lines are listed in Table 3. The $\alpha_1\alpha_2$-doublet is separated for $\sin\theta > 0{\cdot}4$. The calculated sine squares refer to the α_1 component, the observed sine squares correspond to the peak positions of the doublet for $\sin\theta < 0{\cdot}4$.

Determination of the structure

Reflections do not appear if $H+K+L$ is odd; but there are no other systematic absences. Accordingly the space group is $I2$, Im or $I2/m$. The holohedral group, $I2/m$, was assumed to be the correct one, and the success achieved on this basis justifies the validity of the assumption.

The complete structure can be, and indeed was, determined by means of simple intensity arguments such as were used in structure analysis thirty years ago. However, the statistical method based upon the relation

$$S_{H+H'} = S_H S_{H'} \tag{2}$$

(see Zachariasen, 1952), (which formalizes procedures of thirty years ago) also leads to a complete solution and is easier to describe.

If the origin in the space group $I2/m$ is chosen in a twofold inversion center, it is permissible to choose two structure factor signs at will provided one corresponds to odd K and the other to K even with H and K odd. Accordingly, the signs of the strong reflections $(12\bar{5})$ and (334) were assumed to be positive.

The relation (2) was assumed to be valid for all strong reflections (*i.e.* with unitary structure factor greater than 0·30).

The three strongest diffraction lines in the pattern are all composite reflections. These are $(321)+(103)+(132)$, $(22\bar{2})+(23\bar{1})$ and $(32\bar{1})+(10\bar{3})+(013)$. Careful position measurements show that (132), $(23\bar{1})$ and (013) are minor components of these lines. The intensity of the first of these lines is so great that both (321) and (103) must be strong reflections. Similarly, in the cases of the third line, the intensity cannot be due only to the reflection $(10\bar{3})$, and it is hence overwhelmingly probable that $(32\bar{1})$ as well as $(10\bar{3})$ have unitary structure factors above 0.30. Accordingly (321), (103), $(22\bar{2})$, $(32\bar{1})$, $(10\bar{3})$ were included in the list of strong reflections, and it was assumed that $|F_{321}| = |F_{103}|$, $|F_{32\bar{1}}| = |F_{10\bar{3}}|$.

Table 4. *Structure factor signs for strong reflections*

HKL	Sign	*HKL*	Sign	*HKL*	Sign	*HKL*	Sign
040	+	321	+	600	+	$50\bar{3}$	*a*
042	+	$33\bar{4}$	(+)	$64\bar{2}$	+	$54\bar{1}$	*a*
053	+	334	+	642	+	552	*a*
080	+	361	+	$72\bar{3}$	+	$10\bar{3}$	*b*
$13\bar{2}$	+	$37\bar{2}$	+	103	*a*	222	*b*
$12\bar{5}$	(+)	372	+	141	*a*	215	*b*
170	+	$41\bar{1}$	+	$22\bar{2}$	(*a*)	262	*b*
$17\bar{2}$	+	$40\bar{4}$	+	231	*a*	503	(*b*)
$24\bar{4}$	+	$45\bar{1}$	+	$26\bar{2}$	*a*	541	*b*
244	+	$44\bar{4}$	+	424	*a*	$62\bar{2}$	*b*
$32\bar{1}$	+	444	+	471	*a*	044	*ab*

Using equation (2) 26 strong reflections come out with positive structure factors, the structure factor sign of 10 additional strong reflections can be expressed in terms of symbol a (where $a = +1$ or -1), seven in terms of symbol b and one as ab. This set of self consistent structure factor signs is given in Table 4.

The correct choice of signs for the symbols a and b was found from three-dimensional Fourier syntheses based upon the 44 strongest reflections. Only the combination $a = -1$, $b = +1$ gave a reasonable electron distribution with 34 outstanding maxima of approximately the same density.

The coordinates of these maxima were used as starting point for a least square refinement with the Busing–Levi IBM-704 program. The Thomas Hartree f-curve for plutonium was assumed with Roof's empirical values (Roof, 1961) for the anomalous dispersion correction. The temperature factor was taken to be isotropic with $B = 0{\cdot}50$ Å^2.

The refinement was based only upon experimental structure factors for uniquely indexed reflections (marked by asterisks in Table 3). An R-factor of 0·12 was obtained, and this is as low a value as is physically significant in view of quality of the underlying data.

The positions of the atoms are (all with $(000)(\frac{1}{2}\frac{1}{2}\frac{1}{2})+$):

Type	No.	Coordinates
I	2	(000)
II	4	$\pm(x0z)$
III	4	$\pm(x0z)$
IV	4	$\pm(x0z)$
V	4	$\pm(\frac{1}{2}y0)$
VI	8	$\pm(xyz)(x\bar{y}z)$
VII	8	$\pm(xyz)(x\bar{y}z)$

The final parameter values are shown in Table 5.

As a final demonstration of the correctness of the deduced structure Table 6 gives the complete list of reflections with calculated and observed intensities. When no value is given for the observed intensity, it means that it is not possible to tell from the diffraction pattern whether the reflection is weak or absent because of overlap of stronger reflections.

Table 5. *Position parameters*

Type	x	y	z
I	0	0	0
II	$0{\cdot}146 \pm 0{\cdot}004$	0	$0{\cdot}387 \pm 0{\cdot}005$
III	$0{\cdot}337 \pm 0{\cdot}004$	0	$0{\cdot}082 \pm 0{\cdot}005$
IV	$0{\cdot}434 \pm 0{\cdot}004$	0	$0{\cdot}672 \pm 0{\cdot}005$
V	$0{\cdot}500$	$0{\cdot}220 \pm 0{\cdot}003$	0
VI	$0{\cdot}145 \pm 0{\cdot}003$	$0{\cdot}268 \pm 0{\cdot}002$	$0{\cdot}108 \pm 0{\cdot}003$
VII	$0{\cdot}167 \pm 0{\cdot}003$	$0{\cdot}150 \pm 0{\cdot}002$	$0{\cdot}753 \pm 0{\cdot}004$

The structure

A projection of the structure on the Y-plane is shown in Fig. 2. All bond distances below 3·85 Å are listed

Table 6. *Complete list of reflections*

	$\sin^2\theta$ (calc.)		Intensity	
HKL	83°	252°	calc.	obs.
110	0·0125	0·0123	0	0
011	0·0152	0·0151	2	0
10$\bar{1}$	0·0160	0·0159	1	0
101	0·0175	0·0170	1	0
020	0·0219	0·0218	0	0
200	0·0280	0·0275	0	0
12$\bar{1}$	0·0379	0·0377	1	0
002	0·0389	0·0385	0	0
121	0·0393	0·0388	1	0
21$\bar{1}$	0·0418	0·0414	0	0
211	0·0447	0·0437	5	trace
220	0·0499	0·0492	2	0
11$\bar{2}$	0·0500	0·0496	0	0
112	0·0529	0·0519	0	0
130	0·0562	0·0558	2	trace
031	0·0589	0·0586	0	0
022	0·0608	0·0602	0	0
20$\bar{2}$	0·0640	0·0637	11	15
310*	0·0685	0·0672	10	11
202*	0·0698	0·0682	30	28
30$\bar{1}$	0·0706	0·0697	1	0
301	0·0749	0·0731	0	0
23$\bar{1}$	0·0858	0·0849	46	318
22$\bar{2}$	0·0859	0·0855	272	
040*	0·0875	0·0070	87	66
231*	0·0884	0·0872	112	121
222*	0·0917	0·0900	68	67
32$\bar{1}$	0·0924	0·0915	101	200
10$\bar{3}$	0·0924	0·0917	38	
013	0·0931	0·0920	43	
13$\bar{2}$*	0·0937	0·0931	86	82
321	0·0968	0·0949	246	442
103	0·0968	0·0951	160	
132	0·0966	0·0954	18	
31$\bar{2}$	0·1030	0·1023	43	82
14$\bar{1}$	0·1035	0·1029	64	
141*	0·1049	0·1041	52	43
312*	0·1118	0·1090	19	14
400*	0·1120	0·1098	24	29
330*	0·1122	0·1107	27	30
12$\bar{3}$*	0·1143	0·1135	7	7
240*	0·1155	0·1145	14	11
21$\bar{3}$*	0·1167	0·1161	20	21
123*	0·1186	0·1168	17	21
41$\bar{1}$*	0·1243	0·1226	51	51
213	0·1254	0·1228	2	0
042*	0·1264	0·1255	58	45
411*	0·1301	0·1271	5	5
420	0·1339	0·1315	0	0
033*	0·1368	0·1355	8	7
150	0·1437	0·1428	13	11
30$\bar{3}$	0·1441	0·1433	1	
40$\bar{2}$	0·1451	0·1438	3	5
051	0·1464	0·1456	0	0
33$\bar{2}$	0·1468	0·1459	0	0
24$\bar{2}$*	0·1515	0·1508	3	4
332	0·1555	0·1526	5	6
004	0·1557	0·1539	0	0
402	0·1571	0·1528	10	24
303	0·1567	0·1534	4	
242	0·1573	0·1552	0	0
34$\bar{1}$	0·1580	0·1568	0	0
23$\bar{3}$*	0·1604	0·1597	2	3
341	0·1624	0·1601	0	0
11$\bar{4}$*	0·1653	0·1639	5	6
32$\bar{3}$	0·1659	0·1651	0	0
42$\bar{2}$	0·1670	0·1655	1	0
43$\bar{1}$*	0·1680	0·1661	5	6
233*	0·1692	0·1663	10	14
114	0·1711	0·1684	3	0
25$\bar{1}$	0·1739	0·1719	5	4
431	0·1738	0·1706	1	0
251	0·1758	0·1742	2	0
024	0·1776	0·1756	4	6
323	0·1786	0·1751	0	10
422	0·1790	0·1745	13	
20$\bar{4}$	0·1779	0·1769	5	5
510	0·1805	0·1770	2	0
14$\bar{3}$	0·1799	0·1787	0	0
50$\bar{1}$*	0·1811	0·1784	10	11
15$\bar{2}$	0·1811	0·1802	1	0
152	0·1840	0·1824	1	20
143	0·1842	0·1821	11	
501	0·1884	0·1840	0	0
204	0·1895	0·1858	1	0
41$\bar{3}$	0·1964	0·1951	1	
060*	0·1968	0·1958	13	9
440	0·1995	0·1968	3	
350	0·1997	0·1978	0	0
22$\bar{4}$*	0·1998	0·1987	6	10
52$\bar{1}$	0·2030	0·2001	0	0
13$\bar{4}$	0·2090	0·2074	0	0
521*	0·2102	0·2057	13	13
224	0·2114	0·2075	2	0
51$\bar{2}$	0·2122	0·2099	0	0
413	0·2138	0·2085	1	0
16$\bar{1}$*	0·2128	0·2117	8	7
161*	0·2142	0·2128	4	11
134	0·2148	0·2119	1	
31$\bar{4}$*	0·2155	0·2144	5	11
053	0·2243	0·2225	23	19
260	0·2248	0·2233	0	
530	0·2242	0·2206	0	
512*	0·2267	0·2211	8	10
34$\bar{3}$	0·2315	0·2303	1	0
44$\bar{2}$	0·2326	0·2308	1	0
314	0·2329	0·2278	0	0
35$\bar{2}$	0·2342	0·2339	1	0
062*	0·2357	0·2343	6	7
43$\bar{3}$	0·2401	0·2386	3	0
352	0·2430	0·2406	0	25
044*	0·2432	0·2409	26	
343	0·2442	0·2404	4	
442	0·2446	0·2398	0	
10$\bar{5}$	0·2467	0·2445	2	0
25$\bar{3}$	0·2479	0·2476	1	0
015	0·2488	0·2458	0	0
600*	0·2520	0·2471	29	26
50$\bar{3}$*	0·2517	0·2498	22	29
105	0·2540	0·2501	2	
45$\bar{1}$*	0·2555	0·2531	21	18
53$\bar{2}$	0·2559	0·2534	5	14
253*	0·2566	0·2533	12	
433	0·2575	0·2520	7	12
40$\bar{4}$*	0·2561	0·2547	17	20
33$\bar{4}$*	0·2592	0·2579	17	20
26$\bar{2}$*	0·2608	0·2595	21	17
451	0·2613	0·2586	1	
61$\bar{1}$	0·2629	0·2588	4	8
24$\bar{4}$*	0·2654	0·2639	13	20
262*	0·2666	0·2640	27	29
36$\bar{1}$	0·2673	0·2655	12	
54$\bar{1}$*	0·2686	0·2654	43	45
12$\bar{5}$*	0·2686	0·2667	46	45
532	0·2704	0·2647	2	
21$\bar{5}$	0·2696	0·2678	7	
611	0·2716	0·2655	2	
361*	0·2717	0·2689	32	32
503*	0·2735	0·2665	20	24
620	0·2739	0·2689	3	
52$\bar{3}$	0·2736	0·2715	8	
170*	0·2748	0·2734	9	16
541*	0·2758	0·2710	17	13
125*	0·2758	0·2718	11	12
334*	0·2767	0·2713	34	27
244*	0·2770	0·2729	9	15
071	0·2776	0·2761	0	
42$\bar{4}$	0·2780	0·2765	4	
404	0·2794	0·2726	3	
60$\bar{2}$	0·2822	0·2789	0	0
215*	0·2841	0·2790	10	14
16$\bar{3}$*	0·2892	0·2875	9	7
035	0·2925	0·2894	2	0
163	0·2936	0·2909	2	0
523	0·2954	0·2882	2	0
30$\bar{5}$	0·2955	0·2938	0	0
15$\bar{4}$	0·2965	0·2955	0	0
602	0·2996	0·2923	2	0
424*	0·3012	0·2943	10	9
154	0·3023	0·2999	0	0
62$\bar{2}$*	0·3041	0·3007	8	8
27$\bar{1}$	0·3041	0·3025	2	0
63$\bar{1}$	0·3066	0·3024	1	0
271	0·3070	0·3048	2	0
460	0·3088	0·3056	1	0
550	0·3117	0·3074	0	0
17$\bar{2}$*	0·3123	0·3107	7	7
23$\bar{5}$	0·3133	0·3113	0	
631	0·3153	0·3091	1	0
172	0·3152	0·3129	0	0
305	0·3172	0·3106	0	0
32$\bar{5}$	0·3173	0·3156	1	0
622	0·3215	0·3141	1	0
51$\bar{4}$	0·3217	0·3196	0	0
235	0·3278	0·3225	0	0
45$\bar{3}$	0·3276	0·3266	1	0
370	0·3308	0·3283	4	0
61$\bar{3}$	0·3320	0·3291	0	0
14$\bar{5}$	0·3341	0·3315	3	0
325*	0·3391	0·3324	6	15
54$\bar{3}$	0·3392	0·3367	2	
640	0·3395	0·3342	3	
145	0·3414	0·3371	2	0
36$\bar{3}$	0·3409	0·3391	0	0
46$\bar{2}$	0·3419	0·3396	4	0
55$\bar{2}$	0·3433	0·3414	1	
453	0·3449	0·3400	0	
44$\bar{4}$*	0·3436	0·3417	36	42
41$\bar{5}$	0·3463	0·3444	1	
70$\bar{1}$	0·3477	0·3421	2	
35$\bar{4}$	0·3467	0·3459	3	
710	0·3485	0·3418	4	8
514*	0·3507	0·3420	5	5
080*	0·3498	0·3481	14	8
006	0·3504	0·3462	2	
064	0·3525	0·3497	2	0
462	0·3539	0·3485	0	0
363	0·3535	0·3492	0	0
073	0·3554	0·3530	0	0
613	0·3581	0·3492	0	0
701	0·3578	0·3499	0	0
552*	0·3579	0·3516	7	11
11$\bar{6}$	0·3585	0·3551	0	0
543	0·3610	0·3535	4	0

Table 6 (*cont.*)

	sin² θ (calc.)		Intensity	
HKL	83°	252°	calc.	obs.
354	0·3641	0·3593	0	0
444*	0·3668	0·3596	8	8
$37\bar{2}$*	0·3654	0·3634	19	14
$53\bar{4}$	0·3655	0·3632	1	
$18\bar{1}$	0·3658	0·3640	1	
116	0·3672	0·3618	3	
181	0·3673	0·3651	0	0
$72\bar{1}$	0·3695	0·3638	1	0
$64\bar{2}$*	0·3697	0·3659	9	14
$20\bar{6}$	0·3697	0·3670	4	
026	0·3723	0·3679	1	0
372*	0·3741	0·3701	6	9
415	0·3753	0·3668	0	
$26\bar{4}$	0·3747	0·3727	3	0
$63\bar{3}$	0·3760	0·3726	2	0
$71\bar{2}$	0·3774	0·3724	0	0
$56\bar{1}$	0·3779	0·3742	1	0
280	0·3778	0·3756	0	0
721	0·3795	0·3716	5	0
$27\bar{3}$*	0·3791	0·3772	7	6
055	0·3800	0·3764	3	
$34\bar{5}$	0·3829	0·3808	0	
561	0·3852	0·3798	0	0
264	0·3863	0·3817	0	0
642*	0·3871	0·3793	21	26
206	0·3871	0·3804	10	
$47\bar{1}$	0·3867	0·3836	1	
273	0·3878	0·3839	5	
082	0·3888	0·3865	0	0
$43\bar{5}$	0·3900	0·3879	1	0
$60\bar{4}$	0·3903	0·3876	1	0
730	0·3922	0·3853	4	17
471*	0·3925	0·3881	9	
$22\bar{6}$	0·3941	0·3888	5	
534	0·3945	0·3855	2	
$72\bar{3}$*	0·4372	0·4329	10	18
046	0·4379	0·4332	3	

* Uniquely indexed reflections.

Table 7. *Bond distances in β-plutonium*

Bond	No.	Length
I–VII	4	2·97 Å
–III	2	3·15
–VI	4	3·20
–II	2	3·26
Mean	12	3·13 Å
II–III	1	3·03 Å
–VI	2	3·10
–I	1	3·26
–VII	2	3·26
–II	1	3·29
–V	2	3·36
–IV	1	3·39
–VII	2	3·42
–VI	2	3·55
Mean	14	3·31 Å
III–IV	1	2·79 Å
–V	2	2·84
–II	1	3·03
–I	1	3·15
–III	1	3·32
–VI	2	3·32
–VII	2	3·35
–IV	1	3·37
–VI	2	3·43
Mean	13	3·20 Å
IV–III	1	2·79 Å
–IV	1	3·00
–VII	2	3·01
–VI	2	3·16
–VI	2	3·33
–III	1	3·37
–II	1	3·39
–V	2	3·48
Mean	12	3·21 Å
V–VII	2	2·80 Å
–III	2	2·84
–II	2	3·36
–VI	2	3·40
–VI	2	3·46
–IV	2	3·48
–VII	2	3·63
Mean	14	3·28 Å
VI–VI	1	2·91 Å
–VII	1	3·05
–II	1	3·10
–VI	1	3·10
–IV	1	3·16
–I	1	3·20
–III	1	3·32
–IV	1	3·33
–VII	1	3·36
–V	1	3·40
–III	1	3·43
–V	1	3·46
–VII	1	3·48
–II	1	3·55
Mean	14	3·28 Å
VII–VII	1	2·59 Å
–V	1	2·80
–I	1	2·97
–IV	1	3·01
–VI	1	3·05
–VII	1	3·14
–II	1	3·26
–III	1	3·35
–VI	1	3·36
–II	1	3·42
–VI	1	3·48
–V	1	3·63
Mean	12	3·17 Å

in Table 7. The bond lengths are calculated for pure plutonium at 93 °C., and the probable error is ± 0·06 Å. Since there are no interatomic distances in the range 3·63–3·85 Å, the former value is fairly well defined as the extreme radius of the first coordination sphere. The coordination numbers, n, and the mean bond lengths for the various plutonium atoms are also given in Table 7. Assuming a 0·7% increase in bond length in going from $n=12$ to $n=13$ and 1·4% increase from $n=12$ to $n=14$ one deduces a metallic radius of 1·60 Å for plutonium for $n=12$.

Table 8. *Metallic radius*

($n=12$)

Phase	Temperature	Radius	Radius at room temperature
α	25 °C.	1·58 Å	1·58 Å
β	93	1·60	1·59
γ	235	1·601	1·589
δ	320	1·640	1·644
δ′	465	1·638	1·644
ε	490	1·622	1·594

The results as to metallic radius obtained for the various phases of plutonium are given in Table 8. It is seen that the plutonium radius in the δ-phases is appreciably greater than in the four other forms.

It has been shown elsewhere (Zachariasen, 1961) that the 'normal' plutonium radius of 1·59 Å (found

Table 9. *Short and long bonds in α- and β-plutonium*

α-Plutonium

	Short		Long	
Type	No	Range	No.	Range
I	5	2·50–2·76 Å	7	3·38–3·51 Å
II	4	2·62–2·66	10	3·36–3·64
III	4	2·56–2·67	10	3·17–3·53
IV	4	2·55–2·67	10	3·17–3·52
V	4	2·55–2·72	10	3·32–3·54
VI	4	2·56–2·72	10	3·34–3·64
VII	4	2·50–2·73	10	3·34–3·55
VIII	3	2·73–2·76	13	3·21–3·55

β-Plutonium

	Short		Long	
Type	No.	Range	No.	Range
I	4	2·97 Å	8	3·15–3·26 Å
II	3	3·03–3·10	11	3·26–3·55
III	4	2·79–3·03	9	3·15–3·43
IV	4	2·79–3·01	8	3·16–3·48
V	4	2·80–2·84	10	3·36–3·63
VI	4	2·91–3·10	10	3·16–3·55
VII	5	2·59–3·05	7	3·14–3·63

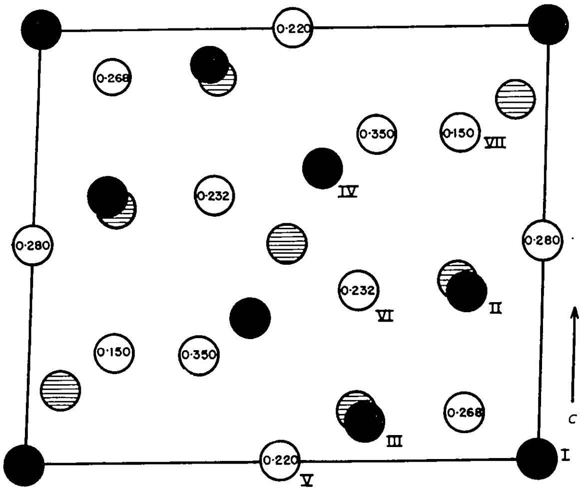

Fig. 2. Shows the structure projected on the Y-plane. Filled circles represent atoms with $y = 0$, shaded circles atoms with $y = 0{\cdot}50$. The numbers within the open circles give the y-coordinates for atoms at heights ± above the projection plane.

in α, β, γ, ε-Pu) corresponds to a valence of $v = 5{\cdot}0$ with 3·0 electrons in the non-bonding 5*f* subshell, and it has been suggested that the 'anomalous' radius observed in the δ-phases may be due to demotion of about 0·4 electron from the valence shell to the 5*f* shell. Similarly, the negative thermal expansion of the δ-phase could be accounted for if the number of 5*f* electrons decreased from 3·4 at 320 °C. to 3·0 at 465 °C.

The data of Table 7 show the existence of a number of short bonds. In the α-plutonium structure there are two sharply defined groups of bonds: 'short' bonds of length 2·50–2·76 Å and 'long' bonds in the range 3·17–3·64 Å, the two classes being separated by a gap of 0·4 Å. As shown in Table 9 the corresponding classification into 'short' and 'long' bonds is much less convincing in the β-plutonium structure. The bond distances observed in the other plutonium phases are given in Table 10.

Table 10. *Bond lengths in other plutonium phases*

		Bonds	
Phase	Temperature	No.	Length
γ	235 °C.	4	3·026 Å
		2	3·159
		4	3·288
δ	320	12	3·279
δ′	465	8	3·249
		4	3·327
ε	490	8	3·149

It is not possible to find simple geometrical interrelationships between the α-, β- and γ-structures.

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