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The Crystal Structure of Alpha Plutonium Metal*

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Alpha plutonium is monoclinic with 16 atoms in the unit cell which at 21 °C has dimensions

$$a = 6{\cdot}183,\ b = 4{\cdot}822,\ c = 10{\cdot}963\ \text{Å};\ \beta = 101{\cdot}79°.$$

The space group is $P2_1/m$, and all atoms lie in reflection planes.

The atomic position parameters have been determined to a precision of 0·03 Å. Six of the eight kinds of plutonium atom form four short bonds of length 2·57–2·78 Å and ten long bonds of length 3·19–3·71 Å. Five short and seven long bonds are formed by the seventh plutonium atom, and three short and thirteen long bonds by the eighth atom.

Introduction

Alpha plutonium is the designation used for the room-temperature form of the element. The phase is stable up to 122 °C, where it transforms to the monoclinic beta modification. No evidence of a phase change at low temperatures has been found.

Several years ago we reported the preliminary findings of a crystal structure investigation of alpha plutonium metal (Zachariasen & Ellinger, 1957). Our subsequent work has led to but minor revisions of the original results, and in this paper we give a final account of our study.

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

Because of the low symmetry of alpha plutonium and because the structure had to be deduced entirely from X-ray powder diffraction data, we have deemed it advisable to describe in some detail the various steps in the investigation. Considerable space is required to give a convincing account of the procedure used to index the diffraction pattern. This step of our study is therefore described in a separate companion article (Zachariasen, 1963).

The experimental data

All diffraction patterns on which the structure determination was based were taken with Cu $K\alpha$ radiation. The metal was of 99·9% purity with an

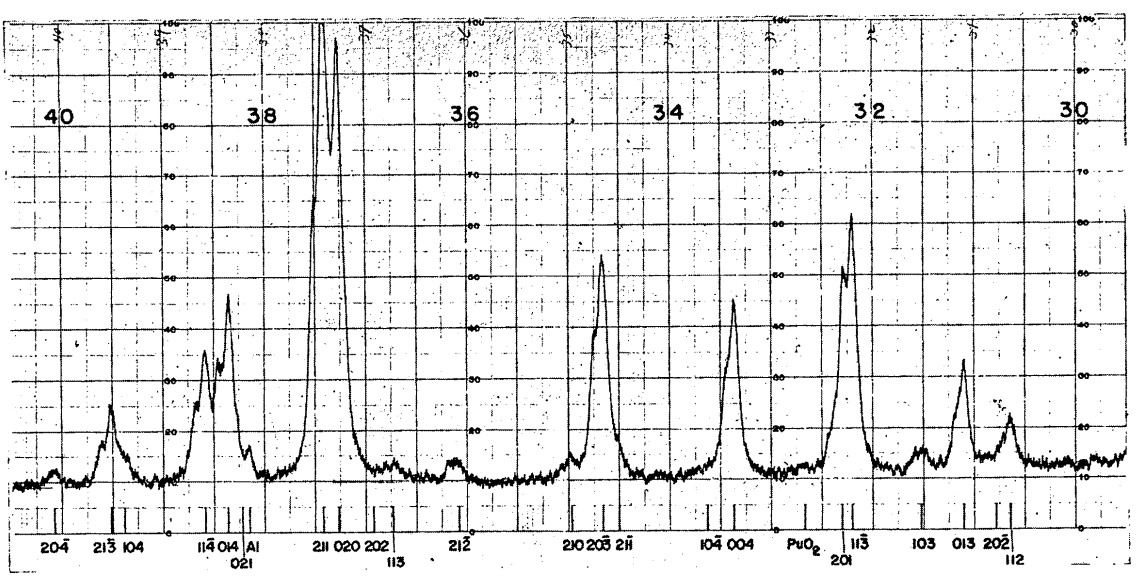

Fig. 1. A typical diffractometer trace in the range $30° < 2\theta < 40°$. The weak line at $2\theta = 38{\cdot}15°$ is due to the incident beam hitting the aluminum frame in which the specimen was held. The calculated positions for all possible diffraction lines are shown.

Table 1. *Diffraction data*
($\sin^2\theta < 0{\cdot}320$)

HKL	$10^5 \sin^2\theta$		Intensity	
	calc.	obs.	obs.	calc.
001	515		0	1·7
100	1619		0	0·4
10$\bar{1}$	1761		0	0·3
002	2061		0	0
101	2507		0	0·7
010	2551		0	0
10$\bar{2}$	2933		0	1·4
011	3066		0	2·8
110	4170		0	1·0
11$\bar{1}$	4312		0	3·9
102	4427		0	1·0
012	4612	4637	7	5·8
003	4637			1·3
111	5058		0	2·4
10$\bar{3}$	5136		0	0
11$\bar{2}$	5484		0	3·3
20$\bar{1}$	6245	6261	7	6·8
200	6477	6482	4	2·2
112	6978	6981	27	33·7
20$\bar{2}$	7045	7043	7	6·8
013	7188	7187	56	56·3
103	7376	7377	13	16·6
11$\bar{3}$	7687	7690	122	128·7
201	7739	7737	64	64·9
004	8243	8244	105	98·4
10$\bar{4}$	8369		?	0·2
21$\bar{1}$	8796	8804	12	13·9
20$\bar{3}$	8874	8878	152	142·1
210	9028	9032	15	11·3
21$\bar{2}$	9596	9601	11	11·6
113	9927	9922	12	10·7
202	10031		<6	1·1
020	10204	10211	246	270·6
211	10290	10290	284	301·4
021	10719		0	0·2
014	10794	10794	121	105·6
11$\bar{4}$	10920	10924	86	72·6
104	11355	11352	15	14·6
21$\bar{3}$	11425	11425	42	39·2
20$\bar{4}$	11734	11737	8	7·7
120	11823		0	0
12$\bar{1}$	11965		0	0
022	12265		0	0
212	12582	12582	25	18·4
10$\bar{5}$	12632	12628		8·4
121	12711		0	0·1
005	12880		0	0·8
12$\bar{2}$	13137		0	0·4
203	13354		0	1·5
114	13906	13900	10	13·2
30$\bar{1}$	13969	13961		3·7
21$\bar{4}$	14285		0?	0
30$\bar{2}$	14395	14399	37	36·0
300	14574	14583	5	3·2
122	14631		0	0·4
023	14841		0	0·6
11$\bar{5}$	15183		0	2·1
12$\bar{3}$	15340		0	0
015	15431	15431	5	2·5
20$\bar{5}$	15624	15633	13	7·5
30$\bar{3}$	15851	15869	16	6·6
213	15905			4·1
301	16209	16208	13	3·6
105	16366	16362	16	10·8
22$\bar{1}$	16449		?	3·4
31$\bar{1}$	16520	16518	13	5·4
220	16681		0	1·2
31$\bar{2}$	16946	16954	19	18·0

HKL	$10^5 \sin^2\theta$		Intensity	
	calc.	obs.	obs.	calc.
310	0·17125	17125	13	11·4
22$\bar{2}$	17249	17257	6	3·9
123	17580	17594	7	5·6
204	17706	17701	17	19·9
10$\bar{6}$	17926	17948	39	2·3
221	17943			38·1
21$\bar{5}$	18175	18169	12	11·1
30$\bar{4}$	18337		?	0·5
31$\bar{3}$	18402		?	1·4
024	18447	18446	70	60·2
006	18547		?	6·1
12$\bar{4}$	18573		?	0
311	18760	18758	3	0·6
302	18875	18923	6	0·3
115	18917			2·2
22$\bar{3}$	19078	19079	95	91·2
222	20235	20259	31	0·8
214	20257			29·3
11$\bar{6}$	20477	20547	8	1·3
20$\bar{6}$	20544			2·5
31$\bar{4}$	20888		<4	0·8
016	21098	21086	17	10·1
312	21426		0?	0·8
124	21559	21558	16	10·8
30$\bar{5}$	21854		0?	0
22$\bar{4}$	21938	21932	10	5·7
106	22406		0?	0·3
303	22571	22563	8	5·0
12$\bar{5}$	22836	22842	11	6·6
030	22960		0	0
025	23084	23091	12	0·6
20$\bar{5}$	23090			0·5
21$\bar{6}$	23095			6·8
031	23475		0	0·2
223	23558		0	1·1
32$\bar{1}$	24173	24233	4	3·1
10$\bar{7}$	24251			1·8
31$\bar{5}$	24405	24405	10	6·1
130	24579	24601	36	0
32$\bar{2}$	24599			30·6
13$\bar{1}$	24721		?	0
320	24778		?	2·6
40$\bar{1}$	24931	24940	8	0·4
116	24957			4·0
40$\bar{2}$	24984			0·2
032	25021		0?	0·5
313	25122	25228	6	0·7
007	25245			2·9
131	25467		0	0·3
215	25641	25630	21	25·2
22$\bar{5}$	25828	25829	11	6·6
13$\bar{2}$	25893		?	0·3
400	25909		?	1·6
32$\bar{3}$	26055	26073	9	5·9
40$\bar{3}$	26066			0·8
30$\bar{6}$	26402	26488	8	5·3
321	26413			3·3
20$\bar{7}$	26496			2·2
125	26570	26573	14	9·8
11$\bar{7}$	26802	26797	21	20·7
304	27297		0?	0·6
13$\bar{2}$	27387		0?	4·3
41$\bar{1}$	27482	27526	52	21·1
41$\bar{2}$	27535			35·0
033	27597			7·4
017	27796	27783	45	41·1
224	27910	27909	30	18·9
401	27917			1·2

Table 1 (*cont.*)

HKL	$10^5 \sin^2\theta$		Intensity	
	calc.	obs.	obs.	calc.
$13\bar{3}$	28096	28090	23	17·8
$12\bar{6}$	28130			2·1
$40\bar{4}$	28179		0?	0·7
$41\bar{0}$	28460		0?	3·0
$32\bar{4}$	28541		0	0·4
$41\bar{3}$	28617	28624	6	0·5
$02\bar{6}$	28751	28759	10	5·8
$31\bar{6}$	28953	28957	55	45·8
$21\bar{7}$	29047		?	2·1
$32\bar{2}$	29079		?	0·3
$23\bar{1}$	29205		?	2·1
230	29437		0	1·9
107	29477		0	0·7
206	29504		0	0·7
314	29848	29839	12	15·2
$23\bar{2}$	30005		?	2·0
133	30336		0	1·9
411	30468	30479	7	1·3
231	30699	30705	61	53·5
$41\bar{4}$	30730		?	3·1
$22\bar{6}$	30748		?	2·7
402	30956		?	1·6
034	31203	31213	24	19·4
$40\bar{5}$	31323	31319	17	0
$13\bar{4}$	31329			13·5
$10\bar{8}$	31605		?	2·4
$23\bar{3}$	31834	31838	12	7·9

Table 2. *Diffraction data*

$(0{\cdot}320 < \sin^2\theta < 0{\cdot}600)$

HKL	$10^4 \sin^2\theta$		Intensity	
	calc.	obs.	obs.	calc.
323	3278	3277	4	5·6
232	3299	3299	7	4·1
305	3305			3·5
$20\bar{8}$	3348	3352	21	3·0
412	3351			20·9
$11\bar{8}$	3416	3414	4	2·5
134	3432	3445	8	3·2
$12\bar{7}$	3446			2·0
$31\bar{7}$	3453			4·4
403	3503	3501	4	4·6
027	3545	3551	11	3·3
018	3552			5·0
$32\bar{6}$	3661	3664	11	6·5
$22\bar{7}$	3670			2·8
$33\bar{2}$	3736	3736	5	5·1
330	3753	3755	8	3·7
413	3758			1·4
108	3758			1·9
$23\bar{5}$	3858	3859	4	3·3
$50\bar{1}$	3913	3913	8	7·2
118	4013			4·2
234	4067	4083	44	9·8
040	4082			31·6
036	4151	4152	5	3·5
$51\bar{1}$	4168	4172	9	7·8
$12\bar{8}$	4181			3·1
501	4287			3·5
$41\bar{7}$	4325	4327	3	2·5
325	4326			4·6
$23\bar{6}$	4350	4351	4	2·5
$22\bar{8}$	4368	4365	5	4·0
$50\bar{5}$	4403	4404	34	23·3
$21\bar{9}$	4404			10·5
423	4523	4541	28	6·4
511	4542			3·5
208	4542			19·9
235	4605	4606	10	10·5
$30\bar{9}$	4623	4623	16	6·3
405	4626			10·8
$13\bar{7}$	4721	4716	11	8·9
128	4778	4792	25	2·8
$43\bar{1}$	4789			9·4
$43\bar{2}$	4794			15·6
037	4821	4818	24	18·5
241	4856	4851	11	8·3
$31\bar{9}$	4878	4879	25	6·4
415	4881			2·8
512	4883			10·8
044	4906	4906	21	13·4
$52\bar{1}$	4934	4936	40	10·3
$33\bar{6}$	4936			21·6
$1,0,\bar{10}$	4941			8·5
$24\bar{3}$	4969	4966	26	21·1
$33\bar{4}$	5026	5026	10	7·4
$1,1,\bar{10}$	5196	5216	4	3·1
144	5217			3·0
521	5307	5306	8	5·5
$2,1,\bar{10}$	5308			5·3
432	5392	5391	13	10·8
$52\bar{5}$	5423	5424	34	37·0
$34\bar{2}$	5521	5521	13	9·8
228	5563	5558	32	32·1
$32\bar{9}$	5643	5642	34	10·3
$24\bar{5}$	5644			2·3
425	5646			17·6
$42\bar{8}$	5714	5712	7	3·9
145	5718			3·5
$3,1,\bar{10}$	5745	5740	8	5·3
600	5830	5829	5	4·0
244	5852	5848	7	7·3
$61\bar{1}$	5912			3·2
$1,2,\bar{10}$	5961	5958	13	14·5

isotopic composition corresponding to an atomic weight of 239·05.

Numerous photographic patterns were made from samples of metal filings, but recordings prepared with a Philips diffractometer proved more useful. Metal buttons with electropolished surface of $1\frac{1}{2}$ cm diameter served as samples for the diffractometer data. The patterns with the greatest resolution were obtained when the polished surface layers of the metal were removed by repeated etching. The quality of the data is illustrated in Fig. 1, which shows an unretouched reproduction of the diffraction pattern for the range $30° \leq 2\theta \leq 40°$. It is seen that diffraction lines of comparable intensity are resolved when the glancing angles differ by as little as 0·05°, and that the $\alpha_1\alpha_2$ doublet begins to resolve into two peaks at $\theta = 18°$.

For the angular range shown in Fig. 1 the scattering angles could be measured to better than 0·01° and hence the maximum error in the experimental values of $\sin^2\theta$ is 5×10^{-5}. In order to get enough intensity at larger scattering angles it was necessary to use wider slits with a corresponding loss of resolution. Altogether about 165 α_1-lines could be measured in the pattern.

The coefficients of thermal expansion were determined from photographic data in the back reflection region. In these experiments the plutonium filings were mixed with powdered silver of high purity. The silver diffraction lines were used to find the correction curve for the measured glancing angles due to finite sample size and absorption.

Only insignificant variations in intensity caused by preferred orientation were noted. Plutonium oxidizes readily, and in spite of precautions it was difficult to avoid oxide formation on the surface. Accordingly, weak and diffuse oxide lines were frequently observed.

The unit cell

All attempts to index the diffraction pattern on the basis of orthorhombic and higher symmetry failed. The companion article describes in detail how the diffraction pattern was indexed in accordance with monoclinic symmetry, and the results of the indexing are shown in the accompanying tables.

In the diffraction pattern of alpha plutonium taken with Cu $K\alpha$ radiation are more than 900 possible diffraction lines. A great many of these are too weak to be observed, and many lines are superimposed.

All possible reflections in the range $\sin^2\theta \le 0{\cdot}320$ are listed in Table 1 together with those actually observed. Table 2 covers the range $0{\cdot}320 \le \sin^2\theta \le 0{\cdot}600$; but all diffraction lines with small *calculated* intensity have been omitted. Data for the strongest diffraction lines (as calculated) in the back reflection region are given in Table 3. The results of measurements of selected strong lines in the back reflection area at different temperatures are shown in Table 4.

The unit cell dimensions as deduced from the data of Table 4 are listed in Table 5. The measured density of 19·77 g.cm^{-3} corresponds to 16 plutonium atoms per unit cell. The calculated densities with this cell content are also shown in Table 5.

The experimental results for the linear coefficients of thermal expansion in the temperature range 21–104 °C are presented in Table 6. The symbols α_a, α_b, α_c are the linear coefficients in the directions of the crystallographic axes while Δ denotes the

Table 3. *Diffraction data*

Back reflection region

HKL	$10^4\sin^2\theta$ calc.	$10^4\sin^2\theta$ obs.	Intensity obs.	Intensity calc.
$71\bar{4}$	7969	7972	110	54
$71\bar{1}$	7980			15
$54\bar{1}$	7995	7994		25
$25\bar{4}$	8148	8150	45	18
$53\bar{8}$	8148			16
710	8190	8192	35	21
419	8363	8364	65	60
$54\bar{5}$	8485	8485	110	108
248	8624	8620	95	102
$25\bar{5}$	8687	8685	210	27
$34\bar{9}$	8704	8705		34
445	8707			58
$3,0,\bar{1}3$	8708			61
$45\bar{1}$	8871	8879	130	28
$45\bar{2}$	8876			47
$05\bar{7}$	8902	8903		57
$35\bar{6}$	9018	9017	130	72
$1,4,\bar{1}0$	9022			56
1,3,11	9102	9102	80	26
$35\bar{4}$	9108			31
$70\bar{8}$	9141	9141	70	45
703	9182	9184	180	38
060	9184			89
616	9283	9283	80	64
452	9473	9479	150	55
$5,1,\bar{1}2$	9483			98
$3,2,\bar{1}3$	9729	9729	300	263

Table 4. *Thermal expansion data*

$10^4\sin^2\theta$

HKL	21 °C calc.	21 °C obs.	51 °C calc.	51 °C obs.	96 °C calc.	96 °C obs.	104 °C calc.	104 °C obs.
419	8363	8364	8341	8343	8307	8308	8297	8297
$54\bar{5}$	8485	8485	8458	8459	8408	8406	8397	8395
248	8623	8620	8599	8599	8556	8550*	8544	8543*
$70\bar{8}$	9141	9141	9115	9116	9072		9067	
703	9182	9184	9152	9152	9101	9099	9090	9077
060	9184		9153		9090		9071	
616	9283	9283	9254	9254	9208	9207	9196	9193
452	9473	9479	9441	9461	9381	9376	9364	9365
$5,1,\bar{1}2$	9483		9461		9428	9427	9424	9422
$3,2,\bar{1}3$	9729	9729	9709	9708	9677	9678	9672	9672
640	9911		9878		9817	9817	9802	9802

* Coincidence with silver line.

Table 5. *Cell dimensions* (Å) *and calculated densities* (g.cm^{-3})

	21 °C	51 °C	96 °C	104 °C
a	6·183 ± 0·001	6·194	6·211	6·214
b	4·822 ± 0·001	4·831	4·847	4·852
c	10·963 ± 0·001	10·973	10·987	10·989
β	101·79 ± 0·01°	101·78°	101·77°	101·75°
ϱ	19·86 ± 0·01	19·77	19·62	19·59

Table 6. *Expansion coefficients*

($\times10^6$)

	21°–51°	21°–96°	21°–104°	Mean 21°–100°
α_a	59	60	60	60 ± 1
α_b	57	69	75	72 ± 3
α_c	30	29	29	29 ± 1
Δ	−6	−5	−8	−7 ± 2
α_1	—	—	—	62 ± 1
α_2	—	—	—	72 ± 3
α_3	—	—	—	29 ± 1
φ	—	—	—	13 ± 2

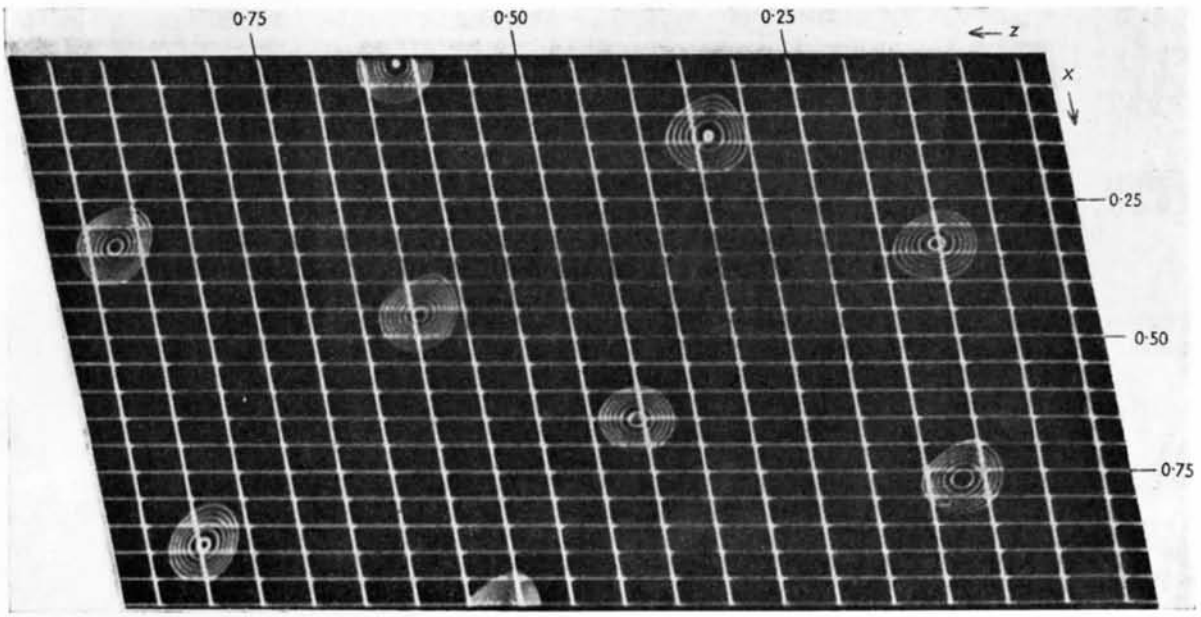

Fig. 2. The generalized projection $\int_0^1 \varrho(1+\sin 2\pi y)\,dy$ as evaluated on XRAC.

change in angle β (measured in radians) per degree rise in temperature. These quantities are related to the principal coefficients α_1, α_2, α_3 and the angle φ describing the orientation of the tensor ellipsoid by the equations (see Zachariasen & Ellinger, 1959)

$$\alpha_1-\alpha_3=-\Delta/\sin\beta\cos(2\varphi-\beta)$$

$$\tan(2\varphi-\beta)=(\alpha_a-\alpha_c)/\Delta$$

$$\alpha_1+\alpha_3=\alpha_a+\alpha_c+\Delta\operatorname{cotan}\beta \quad (1)$$

where φ is the angle between the x-axis of the principal tensor ellipsoid and the crystallographic a-axis measured in the obtuse angle β. It is seen that the direction of minimum expansion (α_3) is nearly parallel to the c-axis.

Determination of the structure

No systematic absences occur for reflections ($H0L$) and (HKL). Reflections (010), (030), (050) are not present, suggesting a screw axis along Y; but the evidence is not conclusive in view of the many accidental absences.

The data of Tables 1–3 show that the condition $|F_{HKL}|/f=|F_{H,K+2,L}|/f$ is fulfilled for any set H, K, L, and that the reflections (020), (040), (060) are exceptionally strong. These observations require the space group to be $P2_1/m$ with all atoms lying in the reflection planes: $\pm(x, \frac{1}{4}, z)$.

Approximate values for the sixteen position parameters of the structure were deduced by means of the probable validity of the relation (see Zachariasen, 1952*a*)

$$S_{H+H'}=S_H S_{H'} \quad (2)$$

for strong reflections (where the symbol S denotes the structure factor sign).

Because of the relation

$$F_{HKL}/f=-F_{H,K+2,L}/f \quad (3)$$

it was sufficient to consider reflections ($H0L$) and ($H1L$). Without loss of generality the structure factor signs for the three strong reflections ($20\bar{3}$), (211), ($50\bar{5}$) were assumed to be positive. By application of equation (2) it was possible to determine uniquely the amplitude signs for 41 strong reflections while the signs for an additional set of 10 strong reflections could be expressed in terms of the symbol b. The results of these considerations are given in Table 7.

Table 7. *Amplitude signs*

$H0L$	sign	$H1L$	sign	$H1L$	sign
004	−	013	+	314	b
0,0,10	$-b$	014	+	$41\bar{2}$	+
0,0,11	+	017	−	$41\bar{1}$	$-b$
1,0,$\bar{1}0$	+	0,1,11	+	412	−
104	−	$11\bar{7}$	+	419	+
105	b	$11\bar{4}$	b*	5,1,$\bar{1}2$	+
$20\bar{5}$	b	$11\bar{3}$	−	$51\bar{9}$	−
$20\bar{3}$	+*	1,1,11	+	$51\bar{8}$	−
201	−	2,1,$\bar{1}0$	+	$51\bar{1}$	+
204	−	$21\bar{9}$	$-b$	512	−
208	+	$21\bar{3}$	−	616	+
3,0,$\bar{1}3$	+	211	+*	$71\bar{4}$	+
$30\bar{2}$	+	214	−	710	−
403	b	215	−		
$50\bar{9}$	−	3,1,$\bar{1}0$	+		
$50\bar{5}$	+*	$31\bar{9}$	+		
$50\bar{1}$	−	$31\bar{7}$	b		
600	b	$31\bar{6}$	−		
$70\bar{8}$	+	$31\bar{2}$	+		

* Sign assumed.

Next, generalized Fourier syntheses

$$\int_0^1 \varrho(1+\sin 2\pi y)\,dy \qquad (4)$$

were evaluated using the signs from Table 7, setting first $b=+1$ and then $b=-1$. The Fourier terms involving the symbol b, being fewer in number and smaller in magnitude, had only a modulating effect on the projection. However, it was immediately apparent that $b=+1$ was the correct choice, for it gave an electron distribution with the required number of eight maxima of nearly equal density.

The approximate atomic positions having been found, additional Fourier terms could be included and successive approximations made. Fig. 2 shows the XRAC photograph of the final generalized electron projection. The coordinates deduced from this Fourier synthesis are those reported in our preliminary communication.

Since the generalized Fourier syntheses utilized only a small number of terms (41 $H0L$ terms and 53 $H1L$ terms), it was to be expected that the least-square method of refinement would give better position parameters.

The least-square refinements were made by using the Busing–Levi IBM-704 program. The Fourier results served as starting point, and an isotropic temperature factor $B=0{\cdot}2$ Å^2 was assumed and not varied in the course of the refinement. For the f-curve of plutonium the effective scattering power, f, was taken to be

$$f=[(f_0-\Delta')^2+\Delta''^2]^{\frac{1}{2}} \qquad (5)$$

where f_0 is the Fermi–Thomas value (Thomas, Umeda & King, 1958) and Δ' and Δ'', the empirical dispersion corrections reported by Roof (1961). The refinements (based on 97 reflections for which the structure factors could be reliably measured) gave $R=0{\cdot}07$ and the parameter values listed in Table 8. The reliability factor and standard errors are as low as the quality of the data justifies.

Table 8. *Position parameters from least-square refinement*

Atom type	x	z
I	$0{\cdot}345\pm0{\cdot}004$	$0{\cdot}162\pm0{\cdot}002$
II	$0{\cdot}767\pm0{\cdot}004$	$0{\cdot}168\pm0{\cdot}002$
III	$0{\cdot}128\pm0{\cdot}004$	$0{\cdot}340\pm0{\cdot}003$
IV	$0{\cdot}657\pm0{\cdot}005$	$0{\cdot}457\pm0{\cdot}003$
V	$0{\cdot}025\pm0{\cdot}005$	$0{\cdot}618\pm0{\cdot}003$
VI	$0{\cdot}473\pm0{\cdot}004$	$0{\cdot}653\pm0{\cdot}002$
VII	$0{\cdot}328\pm0{\cdot}004$	$0{\cdot}926\pm0{\cdot}002$
VIII	$0{\cdot}869\pm0{\cdot}004$	$0{\cdot}894\pm0{\cdot}002$

The last columns of Tables 1–3 give the intensities as calculated from the structure by the relation

$$I \propto p|F|^2(1+\cos^2 2\theta)/\sin^2\theta\cos\theta\,. \qquad (6)$$

It should be emphasized that Tables 2 and 3 include all observed α_1-lines in the pertinent angular ranges and all reflections with appreciable calculated intensity.

Discussion of the structure

The structure as viewed along the b-axis is shown in Fig. 3. The atoms are arranged in pseudo-hexagonal layers normal to the b-axis and 2·411 Å apart. Each atom forms six bonds with atoms in the same reflection plane and six to ten bonds with atoms of adjacent layers. The distortion from hexagonal configuration in the reflection plane is so great that the bond lengths in this plane range from 2·57 to 3·71 Å.

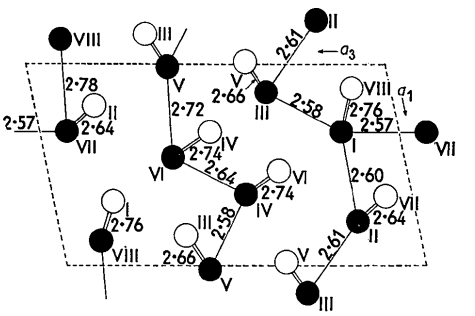

Fig. 3. Projection of the structure on the (010) plane. Filled circles represent atoms at $y=\frac{1}{4}$, open circles atoms at $y=-\frac{1}{4}$. Only the short bonds are indicated in the projection.

Table 9 lists all individual bond distances. Because other interatomic distances exceed 4 Å, the value of 3·71 Å is quite well defined as the extreme radius for the first coordination sphere. It is seen from Table 9 that the various bonds fall naturally into

Table 9. *Individual bond lengths* (Å)

I		II		III		IV	
VII	2·57	I	2·60	I	2·58	V	2·58
III	2·58	III	2·61	II	2·61	VI	2·64
II	2·60	VII	2·64*	V	2·66*	VI	2·74*
VIII	2·76*	VIII	3·19	V	3·24	III	3·26
VI	3·21*	IV	3·37	IV	3·26	III	3·26*
IV	3·41	VII	3·39	IV	3·26*	V	3·32*
VII	3·42*	V	3·42*	IV	3·42	IV	3·35*
II	3·59	VIII	3·46*	VI	3·44*	II	3·37
VIII	3·71	I	3·59	VIII	3·52*	I	3·41
		VI	3·62*	VI	3·65	III	3·42

V		VI		VII		VIII	
IV	2·58	IV	2·64	I	2·57	I	2·76*
III	2·66*	V	2·72	II	2·64*	VII	2·78
VI	2·72	IV	2·74*	VIII	2·78	II	3·19
III	3·24	I	3·21*	VI	3·30	VI	3·21
IV	3·32*	VIII	3·21	II	3·39	V	3·36
VIII	3·36	VII	3·30	VII	3·40*	VII	3·44
II	3·42*	III	3·44*	I	3·42*	II	3·46*
V	3·50*	V	3·51	VIII	3·44	VII	3·48*
VI	3·51	II	3·62*	VIII	3·48*	VIII	3·50*
VII	3·51	III	3·65	V	3·51	III	3·52*
						I	3·71

* Denotes two bonds (with atoms lying in adjacent reflection planes).

two groups: 'short' bonds of length 2·57–2·78 Å and 'long' bonds of length 3·19–3·71 Å. The distribution of the bonds among the two groups for the eight distinct kinds of plutonium atoms is shown in Table 10.

Table 10. *'Short' and 'long' bonds* (Å)

Atom type	Short bonds No.	Short bonds Range	Long bonds No.	Long bonds Range	All bonds No.	All bonds Mean length
I	5	2·57–2·76	7	3·21–3·71	12	3·10
II	4	2·60–2·64	10	3·19–3·62	14	3·21
III	4	2·58–2·66	10	3·24–3·65	14	3·18
IV	4	2·58–2·74	10	3·26–3·42	14	3·13
V	4	2·58–2·72	10	3·24–3·51	14	3·19
VI	4	2·64–2·74	10	3·21–3·65	14	3·22
VII	4	2·57–2·78	10	3·30–3·51	14	3·15
VIII	3	2·76–2·78	13	3·19–3·71	16	3·32

Similar well defined short chemical bonds, presumably of covalent nature, have previously been observed for other heavy metals. In the α-uranium structure (Jacob & Warren, 1937) there are four short bonds of length 2·76–2·82 Å. Four short bonds, 2·60–2·64 Å long, were also found in the structure of α-neptunium (Zachariasen, 1952*b*), and there are four short bonds of length 2·72 Å in β-neptunium (Zachariasen, 1952*c*).

The five short bonds formed by Pu(I) are directed approximately towards the corners of a trigonal bipyramid, the three short bonds of Pu(VIII) approximately towards the corners of an equilateral triangle. As seen from Fig. 3, the four short bonds formed by atoms II–VII tend to lie within one hemisphere, and this is true also for the four short bonds in the uranium and neptunium structures.

The total numbers of bonds (short and long) formed are 12 for Pu(I), 16 for Pu(VIII) and 14 for the six other types of plutonium atoms, and the mean bond lengths are respectively 3·10, 3·32 and 3·18 Å. When corrections are made for the effect of coordination number, these values give 1·58 Å for the metallic radius of plutonium in the α-phase. As has been discussed in detail in another publication (Zachariasen, 1961), the plutonium radius is appreciably smaller in the $\alpha, \beta, \gamma, \varepsilon$ phases than in the δ and δ' phases.

The main features of the observed anisotropy in the thermal expansion can be explained by means of the strong, short bonds. Let it be assumed that all short bonds are of equal strength, let the directions of the bonds be described by unit vectors u_i, and let us form the dyadic $\varphi \equiv \sum_i u_i u_i$ where the sum is extended over all short bonds. The direction s of a principal axis of the tensor is given by the condition that $s.\varphi.s$ be an extremum. The direction of maximum thermal expansion tends to be parallel and the direction of minimum thermal expansion normal to the chemical bonds. Accordingly one should expect the tensor φ and the thermal expansion tensor to have parallel orientations. Indeed, this is true. The quantity $s.\varphi.s$ has its maximum value when s is along the b-axis, its minimum value when s is approximately parallel to the c-axis, and the two long principal axes are of nearly equal length.

It has not been possible to find a simple structural relationship between alpha and beta plutonium, thus indicating that a major rearrangement of the atoms is involved in the $\alpha \rightleftarrows \beta$ transition.

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