Acta Cryst. (1959). **12**, 175

Unit Cell and Thermal Expansion of β-Plutonium Metal

By W. H. Zachariasen

University of Chicago, Department of Physics, Chicago, Illinois, U.S.A. and Consultant to the Los Alamos Scientific Laboratory

and F. H. Ellinger

Los Alamos Scientific Laboratory

(*Received* 25 *September* 1958)

β-Pu is monoclinic body-centered with 34 atoms per unit cell. At 190 °C. $a = 9{\cdot}284$, $b = 10{\cdot}463$, $c = 7{\cdot}859$ Å, $\beta = 92{\cdot}13°$ and the density is 17·70 g.cm.$^{-3}$. Preliminary values are reported for the thermal expansion coefficients.

The β-phase of plutonium metal is stable in the temperature range 122–206 °C. (Coffinberry & Waldron, 1956, p. 372). The $\beta \rightarrow \alpha$-plutonium transition is sluggish, and hence some physical properties of β-plutonium can be measured at temperatures considerably below the transformation point of 122 °C. The addition of 0·5 atomic% zirconium stabilizes the β-phase at room temperature.

The density of pure β-plutonium is reported to be 17·8 g.cm.$^{-3}$ at 150 °C. (Coffinberry & Waldron, 1956, p. 381). Dilatometry measurements give a value of $\bar{\alpha} = 34 \times 10^{-6}$ for the mean linear coefficient of thermal expansion in the interval 133–197 °C. (Coffinberry & Waldron, 1956, p. 375).

The X-ray diffraction pattern of β-plutonium is complex. Attempts to index the pattern on the basis of orthorhombic and higher symmetry failed. A practical method for the interpretation of powder diffraction patterns of monoclinic crystals was developed for the purpose of solving the α-plutonium structure. This method, which will be described in a separate paper, has been successfully applied also to the β-plutonium structure.

The observations used in the interpretation were taken with Cu $K\alpha$ radiation on a General Electric Diffractometer adapted for high-temperature work. Preparations containing small amounts of uranium, cerium or zirconium, as well as samples of pure plutonium, were examined. Intensity variations due to preferential orientation were often observed.

The observed values of $\sin^2\theta$ for β-plutonium correspond to a monoclinic quadratic form with a body-centered translation lattice. The resulting unit-cell dimensions for pure plutonium at 93 °C. and at 190 °C. are shown in Table 1. The observed density requires 34 atoms per unit cell. Conversely, the densities calculated with $n = 34$ are given in Table 1. The only systematic absences are those of the body-centered translation group. Thence, the possible space groups are $I2$, Im and $I2/m$.

Table 1. *Unit cell and density of β-plutonium*

	93 °C.	190 °C.	Accuracy
a	9·227 Å	9·284 Å	±0·003 Å
b	10·449	10·463	±0·004
c	7·824	7·859	±0·003
β	92·54°	92·13°	±0·03°
ϱ	17·91 g.cm.$^{-3}$	17·70 g.cm.$^{-3}$	±0·02 g.cm.$^{-3}$

The first column of Table 2 lists all possible reflections for which $\sin^2\theta < 0{\cdot}140$. The second column gives the calculated values of $\sin^2\theta$ for pure β-plutonium at 190 °C. The next three columns list the observed values of $\sin^2\theta$ for pure plutonium at 190 °C. and at 93 °C. and for a sample containing 0·5 atomic% zirconium stabilized at room temperature. The calculated sine squares for this last sample are shown in the subsequent column and the last column gives the observed intensities for the same sample, which is believed to be relatively free of preferred orientation effects.

So far the diffraction patterns have been completely indexed up to $\sin^2\theta = 0{\cdot}350$. Since there are about two hundred possible reflections in this limited range, it is obviously true that only a small fraction of the reflections are completely resolved.

The data given in Tables 1 and 2 show that there is considerable anisotropy in the thermal expansion. Let α_a, α_b, α_c be the linear expansion coefficients for the three crystallographic axes, and let Δ be the increase in the angle β per degree rise in temperature. Table 3 gives the experimental values of these four quantities in the range 93–190 °C. for pure plutonium, and in the range 133–202 °C. for a plutonium preparation with 1 atomic% cerium added.

Let α_1, α_2, α_3 be the principal components of the expansion tensor. By symmetry one principal axis of the tensor ellipsoid must coincide with the crystallographic b-axis. Thus one may set $\alpha_2 = \alpha_b$. The orientation of the tensor ellipsoid is completely determined by specifying the angle φ which the x-axis of the

Table 2. *Observed and calculated values of* $\sin^2\theta$ *for β-plutonium*

	190 °C.		93 °C.	23 °C.		
hkl	Calc.	Obs.	Obs.	Obs.	Calc.	Int.
110	0·0123	—	—	—	0·0125	—
011	0·0151	—	—	—	0·0152	—
10$\bar{1}$	0·0159	—	—	—	0·0160	—
101	0·0171	—	—	—	0·0175	—
020	0·0217	—	—	—	0·0218	—
200	0·0276	—	—	—	0·0280	—
12$\bar{1}$	0·0377	—	—	—	0·0378	—
002	0·0385	—	—	—	0·0389	—
121	0·0389	—	—	—	0·0393	—
21$\bar{1}$	0·0415	—	—	—	0·0417	—
211	0·0439	—	—	0·0446	0·0447	2
220	0·0493	—	—	—	0·0498	—
11$\bar{2}$	0·0497	—	—	—	0·0499	—
112	0·0521	—	—	—	0·0529	—
130	0·0558	—	—	0·0561	0·0561	2
031	0·0585	—	—	—	0·0588	—
022	0·0603	—	—	—	0·0607	—
20$\bar{2}$	0·0637	0·0638	0·0639	0·0639	0·0639	10
310	0·0676	0·0675	0·0683	0·0684	0·0685	8
202	0·0687	0·0687	0·0697	0·0699	0·0700	20
30$\bar{1}$	0·0699	—	—	—	0·0705	—
301	0·0736	—	—	—	0·0750	—
23$\bar{1}$	0·0849	—	—	—	0·0853	—
22$\bar{2}$	0·0855	0·0855	0·0857	0·0858	0·0857	146
040	0·0870	0·0868	0·0872	0·0874	0·0872	53
231	0·0874	0·0874	0·0879	0·0882	0·0883	60
222	0·0903	0·0903	0·0913		0·0918	
32$\bar{1}$	0·0917	0·0918	0·0922	0·0923	0·0923	183
10$\bar{3}$	0·0918				0·0923	
013	0·0922	—	—		0·0931	
13$\bar{2}$	0·0931	0·0931	0·0932		0·0935	
321	0·0953				0·0968	
103	0·0954	0·0953	0·0964	0·0967	0·0969	201
132	0·0956				0·0965	
31$\bar{2}$	0·1025	0·1027	0·1030	0·1032	0·1028	73
14$\bar{1}$	0·1029				0·1032	
141	0·1041	0·1039	0·1045	0·1047	0·1047	38
312	0·1098	0·1096			0·1120	
400	0·1104	0·1102	0·1117	0·1118	0·1120	53
330	0·1110	0·1109			0·1121	
12$\bar{3}$	0·1135	0·1143	0·1139	0·1149	0·1141	16
240	0·1146		0·1147		0·1152	
21$\bar{3}$	0·1161	0·1161	0·1164	0·1165	0·1165	11
123	0·1172	0·1174	0·1180	0·1187	0·1187	13
41$\bar{1}$	0·1231	0·1231	0·1239	0·1241	0·1241	28
213	0·1234	—	—	—	0·1257	—
042	0·1255	0·1255	0·1259	0·1262	0·1261	29
411	0·1279	0·1281	0·1297	0·1303	0·1302	4
420	0·1322	—	—	—	0·1338	—
033	0·1356	0·1360	0·1372	0·1368	0·1367	5

ellipsoid makes with the crystallographic a-axis in the obtuse angle β. Simple considerations show the following relations between α_1, α_2, α_3, φ and the measured quantities of Table 3:

$$\tan(2\varphi-\beta) = \frac{\alpha_a-\alpha_c}{\Delta}, \quad \alpha_2 = \alpha_b$$

$$\alpha_1-\alpha_3 = -\frac{\Delta}{\sin\beta\cos(2\varphi-\beta)},$$

$$\alpha_1+\alpha_3 = \alpha_a+\alpha_c+\Delta\,\mathrm{cotan}\,\beta\,.$$

The application of these equations to the data of Table 3 gives the results shown in Table 4. The value

Table 3. *Experimental expansion coefficients for β-plutonium*

	93–190 °C.	133–202 °C.
α_a	64×10^{-6}	55×10^{-6}
α_b	14	21
α_c	46	33
Δ	−74	−73

Table 4. *Principal expansion coefficients for β-plutonium*

	93–190 °C.	133–202° C.
α_1	94×10^{-6}	84×10^{-6}
α_2	14	21
α_3	19	7
$\bar{\alpha}$	42	37
φ	40°	38°

found for the angle φ means that the direction of minimum expansion (α_3) is very nearly normal to the plane (10$\bar{1}$).

The determination of the detailed structure of β-plutonium is in progress, but results are not yet available. However, some information about the structure can be deduced from the main features of the diffraction pattern, namely by considering the well known equations for X-ray scattering from a liquid. In the diffraction pattern of β-plutonium there is a heavy concentration of scattered intensity at $\sin\theta \approx 0{\cdot}30$ and there is another one at $\sin\theta \approx 0{\cdot}51$. These intensity maxima imply a predominance of interatomic distances at about 3·3 Å which corresponds to twice the metallic radius of plutonium. There is a secondary intensity maximum at $\sin\theta \approx 0{\cdot}35$, which implies that 2·7 Å may be another prominent interatomic distance in the structure. This suggests the existence of short covalent bonds such as have been found in α-U, α-Np, β-Np and α-Pu.

Reference

COFFINBERRY, A. S. & WALDRON, M. B. (1956). *Progress in Nuclear Energy*, Series V, *Metallurgy and Fuels*. Vol. I.