near the minimum, and this is reported to improve the rate of convergence.

The difficulty experienced in refining the $y$ coordinates of atoms near glide planes is inherent in the absence of recorded reflexions of the type ($hkl$) with $h$ odd, and this difficulty would be experienced in Fourier methods as well as in the steepest-descent method.

If accurate observed structure factors were available, together with a suitable transformation to render the minimum in $R$ space spherically symmetrical, then there seems to be no reason why results given by Booth's method of steepest descents should not be of comparable accuracy with those from Fourier methods, even though a complete set of structure factors is not available. In any case it is possible to obtain at least a good approximation to the true crystal structure from a powder photograph only, as is shown by the work in this paper.

I wish to express my thanks to Dr V. Vand for his advice and encouragement in this work, and to Misses B. Edkins and M. Old for help in the computations.

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# Crystal Chemical Studies of the 5*f*-Series of Elements. XV. The Crystal Structure of Plutonium Sesquicarbide

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$Pu_2C_3$ is cubic with eight molecules per unit cell and $a = 8{\cdot}129 \pm 0{\cdot}001$ Å. The calculated density is $\rho = 12{\cdot}70$ g.cm.$^{-3}$ The space group is $I\bar{4}3d$–$T_d^6$. The plutonium atoms are in 16-fold positions with $x = 0{\cdot}050 \pm 0{\cdot}003$. A reasonable structure is obtained with the carbon atoms in 24-fold positions with $y = 0{\cdot}280$.

Each plutonium atom is bonded to nine carbon atoms, three being at a distance of 2·48 Å, three at 2·51 Å, and three at 2·84 Å. The shortest Pu–Pu distance is 3·35 Å. The carbon atoms are bonded together by covalent bonds to form $C_2$ groups.

The first identification of plutonium carbide was reported in 1944. Dr E. F. Westrum submitted for X-ray diffraction study a micro preparation which he had obtained by lithium reduction of plutonium trifluoride in a graphite crucible. The diffraction study showed the presence of three phases in the sample.

One of these phases corresponded exactly to the compound PuO, which had been encountered in earlier work. The second phase had the sodium-chloride type of structure with $a = 4{\cdot}910 \pm 0{\cdot}005$ kX. and was identified as PuC.

The third phase was cubic with a body-centered translation group and $a = 8{\cdot}11 \pm 0{\cdot}01$ kX. On the basis of volume considerations the compound was tentatively identified as $Pu_2C_3$ with eight molecules per unit cell and a calculated density of $\rho = 12{\cdot}70$ g.cm.$^{-3}$. The space group was given as $I\bar{4}3d$.

The corresponding carbide of uranium was not known at the time these results for plutonium sesquicarbide were obtained. Recently the existence of $U_2C_3$ has been reported (Mallett, Gerds & Vaughan, 1950), and some crystal-structure information given. It is clear from the reported results that $U_2C_3$ is isostructural with $Pu_2C_3$. The authors have, however, overlooked the earlier work on the plutonium compound.

It is the purpose of the present paper to describe the crystal-structure determination of $Pu_2C_3$ in some detail. In the preliminary account of the investigation the identification of $Pu_2C_3$ was given as tentative in character. The uncertainty of the identification was later removed,* and the identity is, of course, further confirmed by the recent identification of the isostructural uranium compound.

## Determination of the crystal structure

Table 1 gives the X-ray diffraction data for $Pu_2C_3$ as obtained with Cu $K$ radiation filtered through nickel

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* $Pu_2C_3$ has also been observed at Los Alamos according to a private communication by A. Coffinberry and F. Ellinger.

foil. The observed intensities in the back-reflection region are listed in the last column of Table 2. For these reflections the $\alpha_1$ and $\alpha_2$ components were well separated. The numerical values for the observed intensities in the back-reflection region were obtained with the aid of the known intensity ratio of 2 : 1 for the $\alpha_1$ to $\alpha_2$ components. This procedure is a convenient substitute for the multiple-film technique whenever the $\alpha_1$–$\alpha_2$ doublet is resolved.

Table 1. *Diffraction data for* $Pu_2C_3$

| $\sin^2\theta$ | $\Sigma H_i^2$ | $H_1H_2H_3$ | $I_0$ | $\lvert F\rvert^2P$ |
|---|---|---|---|---|
| 0·0539 | 6 | 211 | *w* | 36 |
| 0·0726 | 8 | 220 | *m*+ | 85 |
| 0·0913 | 10 | 310 | *s* | 85 |
| 0·1285 | 14 | 321 | *m* | 60 |
| 0·1461 | 16 | 400 | *vw* | 8 |
| 0·2012 | 22 | 332 | *m* | 67 |
| 0·2195 | 24 | 422 | *w* | 43 |
| 0·2362 | 26 | 510 | *vs* | 62 |
| | | 431 | | 124 |
| 0·2724 | 30 | 521 | *ms* | 119 |
| — | 32 | 440 | Nil | 1 |
| 0·3085 | 34 | 530 | *w* | 22 |
| 0·3442 | 38 | 611 | *m*− | 20 |
| | | 532 | | 40 |
| 0·3620 | 40 | 620 | *w*− | 14 |
| 0·3797 | 42 | 541 | *s* | 102 |
| 0·4154 | 46 | 631 | *w*+ | 36 |
| 0·4335 | 48 | 444 | *w*+ | 28 |
| 0·4528 | 50 | 710 | *m* | 18 |
| | | 543 | | 36 |
| 0·4877 | 54 | 633 | *vs* | 45 |
| | | 721 | | 90 |
| 0·5051 | 56 | 642 | *s* | 112 |
| 0·5229 | 58 | 730 | *m*− | 42 |
| 0·5587 | 62 | 732 | *s*− | 0 |
| | | 651 | | 81 |
| 0·5766 | 64 | 800 | *w* | 29 |
| 0·5945 | 66 | 741 | *w*+ | 30 |
| 0·6303 | 70 | 653 | *w* | 30 |
| 0·6480 | 72 | 822 | *m* | 53 |
| | | 660 | | 3 |
| 0·6649 | 74 | 831 | *vs* | 75 |
| | | 750 | | 15 |
| | | 743 | | 75 |
| 0·6995 | 78 | 752 | *w* | 28 |

Table 2. *Data for parameter determination*

| $\Sigma H_i^2$ | $H_1H_2H_3$ | $I_c$: $2\pi x=15°$ | $I_c$: 18° | $I_c$: 20° | $I_0$ |
|---|---|---|---|---|---|
| 80 | 840 | 6 | 6 | 3 | 5 |
| 82 | 910 | 19 | 8 | 3 | 8 |
| 86 | 921 | 13 | 0 | 6 | 40 |
| | 761 | 52 | 48 | 39 | |
| | 655 | 7 | 0 | 3 | |
| 88 | 664 | 84 | 82 | 60 | 70 |
| 90 | 754 | 0 | 20 | 42 | 80 |
| | 851 | 42 | 48 | 54 | |
| | 930 | 0 | 8 | 20 | |
| 94 | 763 | 16 | 0 | 8 | 40 |
| | 932 | 48 | 56 | 48 | |
| 96 | 844 | 60 | 40 | 16 | 30 |
| 98 | 853 | 54 | 26 | 6 | 50 |
| | 941 | 54 | 26 | 6 | |
| 102 | 772 | 10 | 36 | 42 | 40 |
| | 10,1,1 | 10 | 14 | 18 | |
| 104 | 862 | 74 | 58 | 64 | 150 |
| | 10,2,0 | 110 | 128 | 100 | |
| 106 | 943 | 0 | 36 | 88 | 60 |
| | 950 | 44 | 50 | 58 | |

It is seen from Table 1 that the observed sine squares correspond to a cubic body-centered translation lattice. The observed sine squares for the three reflections with the highest values of $\Sigma H_i^2$ give the following results for the unit cell constant:

| $\Sigma H_i^2$ | $\sin^2\theta$ | *a* (kX.) |
|---|---|---|
| 102 | 0·9157 | 8·113 |
| 104 | 0·9338 | 8·112 |
| 106 | 0·9514 | 8·114 |

Thus

$$a=8{\cdot}129\pm0{\cdot}001\ \text{Å}\ (8{\cdot}113\pm0{\cdot}001\ \text{kX.}).$$

It is seen that there are systematic absences in addition to those characteristic of the body-centered translation group. These systematic absences are:

I. $H_1H_1H_3$ is absent if $2H_1+H_3=4n+2$.

II. $H_1H_2H_3$ is absent if $H_1$, $H_2$, $H_3$ are all even and $H_1+H_2+H_3=4n+2$.

The absences listed under I are characteristic of the space-group symmetry $I\bar{4}3d\text{–}T_d^6$. The second group of absent reflections corresponds to the 16-fold positions of this space group. These 16-fold positions are:

$$(0,0,0);\quad (\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2})+$$

$$(x,x,\bar{x});\quad (x+\tfrac{1}{4},x+\tfrac{1}{4},x+\tfrac{1}{4});$$

$$(\tfrac{1}{2}+x,\tfrac{1}{2}-x,\bar{x})\nwarrow;\quad (\tfrac{3}{4}+x,\tfrac{1}{4}-x,\tfrac{3}{4}-x)\nwarrow.$$

By symmetry considerations $x$ can be restricted to the range $0\leqslant x\leqslant\frac{1}{8}$. The fact that 400 is very weak and 440 absent requires $x\approx\frac{1}{16}$. An accurate value for $x$ is readily obtained from the back-reflection data.

Table 2 shows the calculated intensities due to the plutonium atoms for $2\pi x=15$, 18 and 20°. The following intensity formula was used:

$$I_c\propto|F|^2P\frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta},$$

where $P$ is the multiplicity factor. On the basis of the results given in Table 2 one finds

$$x=0{\cdot}050\pm0{\cdot}003.$$

The last column of Table 1 shows the values of $|F|^2P$ calculated with $x=0{\cdot}050$. The excellent agreement between observed and calculated intensities is proof that the number and positions of the plutonium atoms in the unit cell have been correctly deduced.

With sixteen plutonium atoms in the unit cell the volume per plutonium atom is 33·5 Å$^3$. The corresponding value for PuC is 30 Å$^3$. In $UC_2$ the volume per uranium atom is 37 Å$^3$, and one would expect practically the same value for the analogous plutonium compound. Thus the observed volume of the unit cell leads to the conclusion that there are one and a half carbon atoms per plutonium atom, i.e. that the compound is $Pu_2C_3$ with eight molecules per unit cell. This gives a calculated density of $\rho=12{\cdot}70$ g.cm.$^{-3}$.

Because of the small scattering power of carbon relative to plutonium there is no hope of determining the carbon positions from intensity considerations.

Accordingly, an attempt will be made to locate the carbon atoms in other ways.

In the space group $I\bar{4}3d$ there are only two ways in which the twenty-four carbon atoms in the unit cell can be distributed among the available positions. Either the carbon atoms occupy the two sets of 12-fold positions without degrees of freedom, or they are in the 24-fold positions with one degree of freedom.

In the former case the closest Pu–C separation is 2·20 Å. This value is so much smaller than the distance 2·46 Å. observed in PuC that this distribution of the carbon atoms must be discarded as unreasonable.

The 24-fold positions for the carbon atoms are:

$$(0, 0, 0);\quad (\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}) +$$
$$(y, 0, \tfrac{1}{4})\curvearrowleft;\ (\tfrac{1}{2}-y, 0, \tfrac{3}{4})\curvearrowleft;\ (\tfrac{3}{4}+y, 0, \tfrac{3}{4})\curvearrowleft;\ (\tfrac{3}{4}-y, 0, \tfrac{1}{4})\curvearrowleft.$$

If the Pu–C distance is to be 2·46 Å or greater, the parameter $y$ must lie in the range $0{\cdot}27 \leqslant y \leqslant 0{\cdot}48$. By symmetry, values $y$ and $\frac{3}{4}-y$ are equivalent so that only the range $0{\cdot}27 \leqslant y \leqslant 0{\cdot}375$ needs to be considered. For $y = 0{\cdot}375$ two carbon atoms occupy the same site, and it is clear that $y$ must be considerably less than $\frac{3}{8}$ if carbon atoms are to be reasonably far apart. Even if $y = 0{\cdot}27$, the C–C separation is only 1·71 Å. It is therefore clear that the carbon atoms are bonded together. If the bonding corresponds to a single bond, one would expect a C–C distance of 1·54 Å, which requires $y = 0{\cdot}28$.

The value $y = 0{\cdot}28$ will be adopted as leading to the most reasonable structure.

## Discussion of the structure

With the parameter values $x = 0{\cdot}050$ and $y = 0{\cdot}280$ the interatomic distances become:

Pu–3 Pu = 3·35 Å
Pu–2 Pu = 3·52 Å
Pu–6 Pu = 3·70 Å
Pu–3 C = 2·48 Å
Pu–3 C = 2·51 Å
Pu–3 C = 2·84 Å

C–1 C = 1·54 Å
C–2 Pu = 2·48 Å
C–2 Pu = 2·51 Å
C–2 Pu = 2·84 Å

In PuC each plutonium atom is bonded to six carbon atoms with Pu–6 C = 2·46 Å. The distances Pu–C in $Pu_2C_3$ are thus quite reasonable. The Pu–Pu distances are all sufficiently large, but it is difficult to state whether or not there is direct Pu–Pu bonding.

It is seen that carbon atoms are bonded together into pairs. The bond distance of 1·54 Å was assumed, and the actual bond length may possibly be a little shorter than assumed.

Thanks are due to Dr E. F. Westrum for the loan of micro preparations of plutonium carbides and Miss Anne Plettinger for having taken the X-ray diffraction patterns.

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# Crystal Chemical Studies of the 5*f*-Series of Elements. XVI. Identification and Crystal Structure of Protactinium Metal and of Protactinium Monoxide

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X-ray diffraction examination shows that Sherman Fried, P. Sellers and R. E. Elson have succeeded in producing protactinium metal by reduction of the tetrafluoride with barium.

Investigations of the micro preparations showed the presence of small amounts of $PaO_2$ and of two other phases not previously encountered. One of these phases is identified as PaO, and the other as Pa metal.

Protactinium metal is tetragonal body-centered with two atoms in a cell of dimensions

$$a_1 = 3{\cdot}925 \pm 0{\cdot}005,\quad a_3 = 3{\cdot}238 \pm 0{\cdot}007\ \text{Å}.$$

The calculated density is $\rho = 15{\cdot}37 \pm 0{\cdot}08$ g.cm.$^{-3}$.

Each metal atom has ten next neighbors, eight at a distance of 3·212 Å and two at 3·238 Å. The metallic radius of protactinium for co-ordination number twelve is 1·63 Å. The results on thorium, protactinium and uranium show that there are no 5*f*-electrons in the metals.

PaO has the sodium chloride type of structure with $a = 4{\cdot}961 \pm 0{\cdot}003$ Å. The calculated density of PaO is $\rho = 13{\cdot}43$ g.cm.$^{-3}$.

The first compounds of protactinium to be prepared and conclusively identified were $PaO_2$, $Pa_2O_5$, $PaCl_4$, PaOS and $PaF_4$ (Zachariasen, 1949, 1950). In all cases the chemical identity was established through interpretation of X-ray diffraction patterns of the micro preparations.