Comparing our structure with that of Zvonkova & Ždanov we see that the sites of the 4 Ag are different, as well as those of the NO_3^- ions, which according to their supposition should be rotating. The parameter of the 32 O ions in (*f*) would be $\frac{3}{8}$ according to them. Neither of these conclusions is valid: the F values calculated for their structure are not in agreement with the observed ones.

The structure of Chou Kung-Du is, apart from the small difference in the parameter x, identical with ours. It came to our knowledge only after completion of our experimental work. Our neutron diffraction results are in any case a very desirable support for the oxygen positions.

The unit cell of the fluorine-containing products has the cell edge $a=9{\cdot}842-9{\cdot}860$ Å, the fluorine content being variable. The cell contains 44–45 anions (O+F). As in the case of Ag_7NO_{11}, it seems that the cages must contain about 12 anions, otherwise they would collapse. At any rate the fluorine-containing samples are more disordered than Ag_7NO_{11}. The relative intensities of the reflexions are somewhat different, but they have not been worked out thoroughly.

Discussion of properties

The crystals show an electrical conductivity similar to that of semiconductors (McMillan, 1962). They are feebly paramagnetic (Prof. Dr W. Klemm, Münster, private communication).

Both these properties can be explained qualitatively by the fact that the structure is defective in anions (oxygen). It is well-known that many oxides, *etc.*, which are good insulators when stoichiometrically correct, are turned into semiconductors by a stoichiometric excess of one constituent. With excess metal, as in the present case, a semiconductor of *n*-type arises.

Some of the electrons are raised from the donor levels to the conduction band, as a result of interaction with the thermally oscillating lattice. This explains the electrical conductivity. The black colour is also explained: absorption of visible light may raise the electrons from the donor levels into the conduction band.

The electrons of the valency bands form a system with compensated spins and thus they cause diamagnetism. At the same time the electrons in the conduction band can be considered as a classical electron gas which contributes a larger paramagnetic and a smaller diamagnetic part to the susceptibility. Thus a very weak (either para- or dia-)magnetism is to be expected.

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The Crystal Structure of Rhombohedral $PuAl_3$

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The crystal structure is reported for $PuAl_3$ single crystals extracted from aluminum–6 at. % plutonium alloys which had been slow-cooled to 930 °C and then quenched to 20 °C. The structure is rhombohedral with $a_r=7{\cdot}879\pm0{\cdot}003$ Å and $\alpha_r=45{\cdot}94°$, $Z=3$ units of $PuAl_3$ per unit cell and probable space group $R\bar{3}m$. The structure can be described as an assembly of close-packed layers each with an Al:Pu atomic ratio of 3:1 and stacked in the sequence *ABABCBCACA* · · · Thus the stacking sequence is appreciably different from that of the earlier-reported hexagonal configuration, *ABCACBA* · · ·, which is produced on heating rhombohedral $PuAl_3$ to 1027 °C.

Recent studies of the aluminum–plutonium binary system have revealed that several polymorphic transformations occur on heating the intermetallic compound $PuAl_3$ (Runnalls, 1962; Runnalls & Boucher, 1965). Earlier work (Runnalls, 1956; Larson, Cromer & Stambaugh, 1957) had indicated that the only stable configuration was hexagonal with small deviations from an ideal 6*H* structure of stacking sequence

ABCACBA... in the $\mathbf{c}_0$ direction. At least three polymorphic configurations have now been found, however, and X-ray powder diffraction data indicate that others may exist.

A nine layer rhombohedral structure labelled $9H$ is stable up to 1027°C, the hexagonal $6H$ configuration from 1027° to 1210°C, and cubic $PuAl_3$ of stacking sequence *ABCA*... from 1210° to the peritectic decomposition temperature near 1400°C. The purpose of this paper is to present data on the structure of $9H$.

Aluminum–plutonium alloys were prepared by reacting plutonium dioxide with liquid aluminum under cryolite (3 NaF . AlF_3) at 1100°C. (Runnalls, 1959). The aluminum used was of 99·99% purity and the plutonium dioxide was 99·8% pure with trace impurities of Ca, Cu, Fe, Pb, Si and Zn. When liquid alloys containing 5·3 to 6·8 at % Pu were cooled at 100°C/h primary crystals of $9H$ $PuAl_3$ were precipitated in the liquid. Once the temperature had been decreased to 930°C the alloys were quenched in water to suppress the peritectic decomposition of $PuAl_3$ to $PuAl_4$. Single crystals were separated from the alloys by dissolving the aluminum matrix in $2N$ NaOH.

A series of oscillation, Weissenberg and precession photographs of the crystals prepared in the above way showed that the primitive cell was rhombohedral with $a_r = 7{\cdot}879 \pm 0{\cdot}003$ Å and $\alpha_r = 45{\cdot}94°$. The calculated density assuming 3 Pu atoms and 9 Al atoms per unit cell was 6·918 g.cm^{-3}, close to the 6·904 g.cm^{-3} calculated for the hexagonal $6H$ phase of dimensions $a_0 = 6{\cdot}083$ and $c_0 = 14{\cdot}410$ Å. A Laue photograph exhibited ditrigonal symmetry identifying the point group as 32, $3m$ or $\bar{3}m$. Since the only systematic extinctions were for $-h+k+l \neq 3n$, the possible space groups are $R32$, $R3m$ and $R\bar{3}m$.

A hexagonal model for the structure of $9H$ consistent with the observed dimensions was constructed using nine close-packed layers each containing one Pu and three Al atoms and stacked in the sequence *ABABCBCACA*... (see Fig. 1). From zero level Weissenberg photographs with Cu $K\alpha$ radiation it was apparent that the layers were not located exactly at $\frac{1}{9}z$ since weak reflections were observed for $00{\cdot}l \neq 9n$. An $h0{\cdot}l$ photograph with Mo $K\alpha$ radiation showed that the intensities of the reflections 00·42 and 00·45 were equal. Assuming that only the Pu atoms contribute appreciably to such high order reflections and with 3 Pu in (a) and 6 Pu in (c) of space group $R\bar{3}m$ the calculated intensities for 00·42 and 00·45 were nearly equal for $z_{Pu} = 0{\cdot}2185 \pm 0{\cdot}0005$. Good agreement between calculated and observed intensities for higher order reflections was evident as well (Table 1).

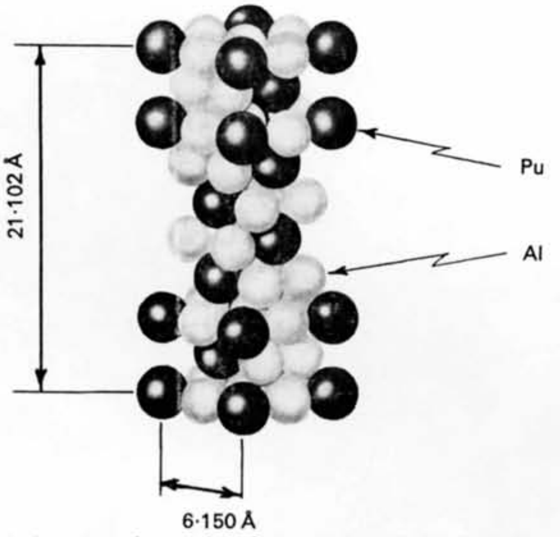

Fig. 1. A perspective model of rhombohedral $PuAl_3$ on hexagonal coordinates.

Table 1. *Intensities of* 00·*l reflections on a zero level Weissenberg photograph of rhombohedral* $PuAl_3$ *for* $z_{Pu} = 0{\cdot}2185$

Radiation: Mo $K\alpha$

l	I(obs)	I(calc)*
42	w^+	5·1
45	w^+	5·3
48	vw	1·3
51	m	7·2
54	w	4·2

* $I \alpha |F_{Pu}|^2 \left\{ \frac{1+\cos^2 2\theta}{\sin 2\theta} \right\}$

Once the Pu positions had been specified, the Al parameters were chosen from the following geometric considerations. It was assumed that in the *ABA* layers for example each Al atom in B would be equidistant from the two Pu atoms in the adjacent A layers. Thus the z_{Al} parameter was set equal to $z_{Pu}/2 = 0{\cdot}1093$. Using the same $Pu_I - Al_{II}$ distance of 3·01 Å as was reported for $6H$ $PuAl_3$ (Larson *et al.*, 1957) and for $3H$ $PuAl_3$ (Runnalls & Boucher, 1965) the calculated x_{Al} parameter then became 0·1815. Therefore the postulated positions in space group $R\bar{3}m$ using hexagonal axes were as follows:

	$(0, 0, 0; \frac{1}{3}, \frac{2}{3}, \frac{2}{3}; \frac{2}{3}, \frac{1}{3}, \frac{1}{3})+$
3 Pu in (a)	$0, 0, 0$
6 Pu in (c)	$0, 0, z; 0, 0, \bar{z}$ with $z = 0{\cdot}2185$
9 Al in (e)	$\frac{1}{2}, 0, 0; 0, \frac{1}{2}, 0; \frac{1}{2}, \frac{1}{2}, 0$
18 Al in (h)	$x, \bar{x}, z; x, 2x, z; 2\bar{x}, \bar{x}, z;$ $\bar{x}, x, \bar{z}; \bar{x}, 2\bar{x}, \bar{z}; 2x, x, \bar{z}$ with $x = 0{\cdot}1815$ and $z = 0{\cdot}1093$.

Calculated intensities were in reasonable agreement with those observed visually in the front reflection region of a film from a Philips camera of 11·46 cm using Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å) as indicated in Table 2. The difference in observed and calculated values of $\sin^2\theta$ in Table 2 compared with the good agreement found in the back reflection region (Runnalls & Boucher, 1965) is an indication of the highly absorbing nature of the specimen.

Table 2. *Powder diffraction data for rhombohedral* $PuAl_3$

Radiation: Cu $K\alpha$

$hk{\cdot}l$	$\sin^2\theta$ (obs)	$\sin^2\theta$ (calc)	I(obs)	I(calc)*
10·1	0·0231	0·0223	*m*	586
01·2	0·0273	0·0263	*w*	185
10·4	0·0434	0·0423	*s*	1000
00·6	—	0·0480	—	3
01·5	0·0555	0·0543	*s*	954
11·0	0·0640	0·0629	*s*	950
11·3	—	0·0749	—	4
02·1	0·0865	0·0851	*m*	309
10·7		0·0863		63
20·2	0·0900	0·0891	*w*	110
02·4	0·1062	0·1052	*s*	732
01·8		0·1064		35
00·9	0·1100	0·1081	*m*	269
11·6	—	0·1109	—	8
20·5	0·1189	0·1172	*s*	711
21·1	0·1502	0·1481	m^-	81
02·7		0·1492		62
21·$\bar{2}$	0·1555	0·1520	w^+	25
01·10		0·1544		98
21·4	0·1704	0·1680	*m*	139
20·8		0·1692		75
11·9	0·1730	0·1710	*s*	715
21·$\bar{5}$	0·1817	0·1800	*m*	162
01·11		0·1824		8
30·0	0·1906	0·1886	*m*	201

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

The calculated interatomic distances for the proposed structure with estimated accuracies of the bond lengths are summarized in Table 3.

All atoms have a coordination number of twelve with twelve Al around each Pu and four Pu plus eight Al around each Al.

Table 3. *Interatomic distances in rhombohedral* $PuAl_3$ *at* 20 °C

Atom	Neighbour	No. of neighbours	Distance
Pu_I	Al_I	6	3·08 ± 0·01 Å
Pu_I	Al_{II}	6	3·01 ± 0·03
Pu_{II}	Al_{II}	6	3·08 ± 0·03
Pu_{II}	Al_{II}	3	3·01 ± 0·03
Pu_{II}	Al_I	3	3·00 ± 0·02
Al_I	Al_I	4	3·08 ± 0·01
Al_I	Pu_I	2	3·08 ± 0·01
Al_I	Pu_{II}	2	3·00 ± 0·02
Al_I	Al_{II}	4	2·87 ± 0·05
Al_{II}	Al_{II}	2	2·80 ± 0·05
Al_{II}	Al_{II}	2	3·35 ± 0·05
Al_{II}	Pu_{II}	2	3·08 ± 0·03
Al_{II}	Pu_I	1	3·01 ± 0·03
Al_{II}	Pu_{II}	1	3·01 ± 0·03
Al_{II}	Al_I	2	2·87 ± 0·03
Al_{II}	Al_{II}	2	2·91 ± 0·05

The excellent agreement between observed and calculated intensities indicates that the structure can be adequately described by positions in space group $R\bar{3}m$. Space group $R32$ is not excluded as a possibility, however, because of the very small effect on calculated intensity of a slight shift in the nine Al atoms from the special positions in $R\bar{3}m$ to the general ones in $R32$.

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