

## The Crystal Structure of PuAl<sub>3</sub>\*

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The crystal structure of PuAl<sub>3</sub> has been determined by single-crystal methods. The structure is hexagonal with  $a = 6.10 \pm 0.02$ ,  $c = 14.47 \pm 0.04$  Å,  $Z = 6$  units of PuAl<sub>3</sub> per unit cell, and most probable space group  $P6_3/mmc$ . The structure is a new type of  $AB_3$  structure and is an example of a type of hexagonal closest packing in which the stacking sequence is  $\dots ABCAUBA\dots$ , rather than  $\dots ABAB\dots$  as in the usual hexagonal closest-packing structure. This structure is related to that of the cubic substance UAl<sub>3</sub> through an ordered rearrangement of the close-packed layers parallel to the (111) plane and a slight distortion of this 'ideal' structure caused by the relative size difference between Pu atoms and Al atoms.

### Introduction

Several years ago one of us (C. K. S.) studied the crystal structure of PuAl<sub>3</sub> and arrived at an approximate structure. It was recently brought to our attention that Runnalls (1953) had worked on this same structure, and he has since published his work (Runnalls, 1956). It was noted that his original model differed from ours in some important details. We decided therefore to repeat and refine our earlier work.

### Experimental

Single-crystal specimens of PuAl<sub>3</sub> were prepared by essentially the same method as that described by Runnalls (1956). Weissenberg photographs were taken of the  $h0l$ ,  $hhl$ ,  $h1l$ ,  $hk0$ , and  $hkl$  reciprocal lattice nets with Cu  $K\alpha$  radiation. These photographs showed the following symmetry:  $h0l$ ,  $hhl$ , and  $h1l$  reciprocal lattice nets,  $C_{2v}$ ;  $hk0$  and  $hkl$  reciprocal lattice nets,  $C_{6v}$ . The only systematic extinction observed was  $hhl$  with  $l$  odd. Possible space groups are  $P6_3/mmc$ ,  $P6_2c$  and  $P6_3mc$ . The lattice constants were determined from measurements on  $h0l$  Weissenberg photographs and found to be

$$a = 6.10 \pm 0.02, \quad c = 14.47 \pm 0.04 \text{ \AA}$$

( $\lambda$  (Cu  $K\alpha_1$ ) = 1.54051 Å), in good agreement with Runnalls (1956). The density was found to be about 6.4 g.cm.<sup>-3</sup> by the displacement method, using bromobenzene as the displacement liquid. Thus  $Z = 5.5$  (6) formula units per unit cell.

A series of single-film timed Weissenberg photographs of the  $h0l$  reciprocal-lattice net was taken with Mo  $K\alpha$  radiation and a crystal about  $0.1 \times 0.1 \times 0.2$  mm., the longer dimension being parallel to the rota-

tion axis. The intensities were visually estimated with the aid of a series of spots of known relative intensity made from the same crystal. Of the approximately 465 possible non-equivalent reflections, 319 were observed. Reflections were observed to the limit of the Mo reflection sphere, indicating a small temperature factor. Intensities were corrected for the  $L.p$  factors and converted to relative structure factors in the usual way. No absorption correction was made because of the irregular shape of the crystal. The excellent agreement between observed and calculated structure factors finally obtained suggests that the absorption error was not serious.

The empirical formulae given in Compton & Allison (1935) were used to calculate the mass absorption coefficient for Pu with Mo  $K\alpha$  radiation. The value of  $\mu/\rho$  obtained in this way was approximately 48. The linear absorption coefficient of PuAl<sub>3</sub> is thus 258 cm.<sup>-1</sup>. Ultimately, the absorption was partially corrected for by the temperature-factor parameters in the least-squares refinement.

### Determination of the structure

Qualitative examination of the intensity data enabled an approximate structure to be found. The  $00l$  reflections are very strong for  $l = 6n$  and, although unquestionably present, are weak if  $l = 2n \neq 6n$ . (Runnalls, 1953, 1956, observed  $00l$  reflections only with  $l = 6n$ .) The Pu atoms (at least) are therefore located in or nearly in layers not quite  $c/6$  apart. The  $h00$  reflections are present only for  $h = 3n$ , indicating that at least the Pu atoms are in layers  $a/3$  apart. Reflection (600) is about as strong as (300), indicating that the Al atoms are probably in layers approximately  $a/6$  apart with two-thirds of the Al atoms in positions such that they scatter X-rays with phases opposite to those scattered by the Pu atoms. From this information an approximate model for the structure, based on

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$P6_3/mmc$ , was obtained, this 'ideal' model being identical with Runnalls' (1953, 1956) structure. The coordinates for this model are given in Table 1. That it is

Table 1. *Atomic positions for approximate structure of PuAl<sub>3</sub>*

2 Pu <sub>1</sub> in (b):	$\pm(0, 0, \frac{1}{4})$
4 Pu <sub>2</sub> in (f):	$\pm(\frac{1}{3}, \frac{2}{3}, z; \frac{1}{3}, \frac{2}{3}, \frac{1}{2}-z); z = \frac{1}{12}$
6 Al <sub>1</sub> in (h):	$\pm(x, 2x, \frac{1}{4}; 2\bar{x}, \bar{x}, \frac{1}{4}; x, \bar{x}, \frac{1}{4}); x = \frac{1}{2}$
12 Al <sub>2</sub> in (k):	$\pm(x, 2x, z; 2\bar{x}, \bar{x}, z; x, \bar{x}, z; \bar{x}, 2\bar{x}, \frac{1}{2}+z; 2x, x, \frac{1}{2}+z; \bar{x}, x, \frac{1}{2}+z); x = \frac{1}{3}, z = \frac{1}{12}$

only an approximation to the correct structure is evident from the fact that *all* 00*l* reflections with  $l = 2n$  were found to be present with the exception of (0,0,34). Further evidence of departure from the ideal model can be found in certain *h*0*l* reflections, because the ideal model would require zero intensity for the following observed reflections: 30*l* with  $l = 1, 3, \dots, 15$ . The presence of these reflections indicates that the *x* parameters of the Al atoms are not quite correct in the ideal model.

The 00*l* reflections provide a means of calculating the *z* parameter of the Pu<sub>2</sub> atoms. If one assumes that only the Pu atoms contribute appreciably to high-order reflections (e.g., for (0,0,36), the ratio of  $f_{\text{Pu}}:f_{\text{Al}}$  is approximately 20:1 without allowance for temperature factors), the high-order 00*l* structure factors take the form

$$F(00l) = 2f_{\text{Pu}}(1 + 2 \cos 2\pi l \Delta); l = 6n,$$

$$F(00l) = -2f_{\text{Pu}}(1 - \cos 2\pi l \Delta + \sqrt{3} \sin 2\pi l \Delta); l = 6n + 2,$$

$$F(00l) = 2f_{\text{Pu}}(1 - \cos 2\pi l \Delta - \sqrt{3} \sin 2\pi l \Delta); l = 6n - 2,$$

where  $\Delta$  is the change in the *z* parameter from the ideal value of  $\frac{1}{12}$ . Thus, if  $\Delta$  is positive, the ratio  $F(0,0,6n)/F(0,0,6n+2)$  will decrease to unity and smaller, and if  $\Delta$  is negative, the ratio  $F(0,0,6n)/F(0,0,6n-2)$  will do likewise. The former ratio becomes less than 1 at the pair (0,0,36)(0,0,38). With this pair an approximate value of  $\Delta$  can be obtained, and thus one finds  $z_{\text{Pu}_2} \approx 0.088$ , or slightly greater than  $\frac{1}{12}$ .

The Al parameters were found from an *h*0*l* Fourier projection, the phases for which had been determined by the Pu atoms. The parameters from the Fourier are given in Table 2.

Table 2. *Parameters in PuAl<sub>3</sub> obtained from the h0l Fourier projection*

	<i>x</i>	<i>z</i>
Pu <sub>1</sub>	0	$\frac{1}{12}$
Pu <sub>2</sub>	$\frac{1}{3}$	0.089
Al <sub>1</sub>	0.511	$\frac{1}{2}$
Al <sub>2</sub>	0.833	0.082

### Least-squares refinement

All calculations for the least-squares refinement were performed on the Maniac. Thomas-Fermi form factors

were used for Pu. Al form factors were taken from the *Internationale Tabellen* (1935). All observations were given equal weight and reflections with  $F_o = 0$  were omitted.

A satisfactory structure based on  $P6_3/mmc$  had been deduced, but the other possible space groups were not excluded. The first least-squares refinement was therefore made using space group  $P6_2c$ . If this space group is used there are 2 Pu in 2(b), 4 Pu in 4(f), 6 Al in 6(h) and 12 Al in 12(i). If  $y = 2x$  for both kinds of Al, the symmetry is that of  $P6_3/mmc$ . The scale factor, separate isotropic temperature factors for Pu and Al and six atomic coordinates were refined simultaneously. All cross-product elements in the  $9 \times 9$  matrix were included. The problem in this form would not converge. The quantities  $(y-2x)$  oscillated from plus to minus, and whenever  $(y-2x)$  for one of the Al atoms became small, unreal changes were observed in the *x* coordinate of that Al atom in the next cycle. The large change occurred because for  $y \approx 2x$ ,  $\partial F/\partial x \approx 0$ .

The question arose whether a problem of this type would converge if *y* were not quite equal to 2*x*, provided the data were very accurate. To answer this question, structure factors were calculated for the case  $y-2x = 0.003$  for both of the Al atoms. These calculated structure factors were used as the observed ones in a least-squares refinement. This artificial problem was found to converge. It was therefore concluded that within the accuracy of our data,  $y = 2x$  for both Al atoms.

The refinement of the structure in space group  $P6_3/mmc$  was then made. Seven parameters were used, the atomic coordinates having been reduced to four by adoption of this space group. The problem quickly converged. Seven cycles were computed although only three cycles were required to reduce all changes to less than their standard deviations. The final value of *R* was 10.9% with  $F_o = 0$  omitted. The final parameters are listed in Table 3. The standard

Table 3. *Scale factor, temperature factors and atomic parameters obtained from the least-squares refinement of PuAl<sub>3</sub>*

Parameter	Using Thomas-Fermi form factor for Pu	Using modified Thomas-Fermi form factor for Pu
Scale factor*	0.0496 $\pm$ 0.0005	0.0532
$B_{\text{Pu}}$ (cm. <sup>2</sup> )	0.572 $\pm$ 0.031 $\times 10^{-16}$	0.366 $\times 10^{-16}$
$B_{\text{Al}}$ (cm. <sup>2</sup> )	0.781 $\pm$ 0.195 $\times 10^{-16}$	0.977 $\times 10^{-16}$
$x_{\text{Al}_2}$	0.8337 $\pm$ 0.0040	0.8335
$z_{\text{Al}_2}$	0.0815 $\pm$ 0.0007	0.0816
$x_{\text{Al}_1}$	0.5160 $\pm$ 0.0030	0.5156
$z_{\text{Pu}_2}$	0.0892 $\pm$ 0.0001	0.0892

\* This scale factor is defined by  $F_o = KF_c$  and is reciprocal to that usually used.

deviations have been computed in the usual manner using the diagonal elements of the inverse matrix. Table 4 gives the final set of observed and calculated structure factors.



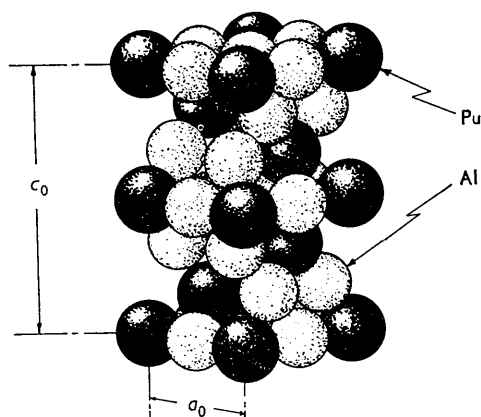


Fig. 1. The 'ideal'  $\text{PuAl}_3$  Structure. (Diagram reproduced with the permission of Runnalls, 1956.)

characteristic of the usual form of hexagonal close packing. Because  $z_{\text{Pu}_2}$  is greater than  $\frac{1}{12}$ , the separation of the planes of Pu atoms in the *A* and *C* layers is less than  $c/12$  while separation of the planes

Table 5. *Interatomic distances in  $\text{PuAl}_3$*

$\text{Pu}_1\text{-Al}_1$	(6)	$3.055 \pm 0.021 \text{ \AA}$	All 6 bonds are coplanar
$\text{Pu}_1\text{-Al}_2$	(6)	$3.007 \pm 0.030$	Trigonal prism coordination about $\text{Pu}_1$
$\text{Pu}_2\text{-Al}_2$	(6)	$3.052 \pm 0.030$	The 6 Al are coplanar but their plane is 0.11 $\text{\AA}$ from $\text{Pu}_2$
$\text{Pu}_2\text{-Al}_2$	(3)	$3.033 \pm 0.030$	These six Al form a distorted octahedron, or a trigonal antiprism, about the $\text{Pu}_2$
$\text{Pu}_2\text{-Al}_1$	(3)	$3.021 \pm 0.021$	
$\text{Al}_1\text{-Al}_1$	(2)	$2.758 \pm 0.030$	All 6 bonds are coplanar
$\text{Al}_1\text{-Al}_1$	(2)	$3.342 \pm 0.030$	
$\text{Al}_1\text{-Pu}_1$	(2)	$3.055 \pm 0.021$	
$\text{Al}_1\text{-Al}_2$	(4)	$2.963 \pm 0.037$	Trigonal prism coordination about $\text{Al}_1$
$\text{Al}_1\text{-Pu}_2$	(2)	$3.021 \pm 0.021$	
$\text{Al}_2\text{-Al}_2$	(4)	$3.054 \pm 0.042$	Four coplanar Al-Al bonds
$\text{Al}_2\text{-Pu}_2$	(2)	$3.052 \pm 0.030$	Two Al-Pu bonds slightly out of this plane
$\text{Al}_2\text{-Al}_1$	(2)	$2.961 \pm 0.037$	Six atoms form a distorted octahedron, or a trigonal antiprism, about the $\text{Al}_2$
$\text{Al}_2\text{-Al}_2$	(2)	$2.941 \pm 0.042$	
$\text{Al}_2\text{-Pu}_1$	(2)	$3.007 \pm 0.030$	

of Pu atoms in the *B* and *C* layers is greater than  $c/12$ . The reverse situation holds for the  $\text{Al}_2$  atoms because  $z_{\text{Al}_2}$  is less than  $\frac{1}{12}$ .

The interatomic distances are given in Table 5. The coordination number of all atoms is twelve. The Pu atoms have twelve Al neighbors and the Al atoms have eight Al and four Pu neighbors.

The  $\text{Pu}_1$  and  $\text{Al}_1$  atoms each have six neighbors in the mirror plane and three above and three below forming a trigonal prism. The  $\text{Pu}_2$  and  $\text{Al}_2$  atoms have six neighbors forming a nearly coplanar arrangement and three above and three below forming a trigonal antiprism or distorted octahedron.

The  $\text{Pu}_2$  atoms are slightly displaced from the plane of the six  $\text{Al}_2$  atoms, probably because of the relative size of the atoms, the Pu atom being slightly larger than the Al atom. The  $\text{Pu}_2$  atom thus causes a spreading apart of the three  $\text{Al}_1$  atoms above. This spreading apart of the three  $\text{Al}_1$  atoms causes three other  $\text{Al}_1$  atoms to approach each other rather closely at a distance of 2.76  $\text{\AA}$ . This Al-Al distance is somewhat shorter than that found in Al metal (2.86  $\text{\AA}$ ) but is similar to the distance found by Runnalls (1956) in  $\text{PuAl}_2$  (2.77  $\text{\AA}$ ).

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