

The Crystal Structure of ζ -Pu–Zr, Ideal Formula $\text{Pu}_{28}\text{Zr}^*$

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Abstract

The crystal structure of the ζ phase in the Pu–Zr system, ideal formula Pu_{28}Zr , has been deduced and refined from the X-ray powder pattern. Refinement was by the pattern-fitting, structure-refinement technique. The space group is $I4_1/a$; there are four formula units in the unit cell with $a = 18.1899$ (3) and $c = 7.8576$ (2) Å at 293 K. The structure has a few features in common with β -Pu. There is one very short interatomic distance of 2.50 Å. The number of neighbors of Pu varies from 12 to 14 while the presumed Zr site has 16 neighbors. However, no direct evidence of Zr ordering was obtained. The average number of valence electrons per atom is 5.2, the same as in γ -Pu.

Introduction

The existence of the Pu–Zr ζ phase at 2–3 at.% Zr has been reported by Ellinger (1961), by Kutaitsev, Chebotarev, Lebedev, Andrianov, Konev & Menshikova (1967) and by Taylor (1969). The isostructural Pu–Hf phase has been reported by Kutaitsev *et al.* (1967) and by Ellinger & Land (1968). Zachariassen & Ellinger (1970), hereafter ZE, indexed an X-ray diffractometer powder pattern of a 3 at.% Zr phase as a body-centered tetragonal cell with $a = 18.19$ and $c = 7.85$ Å. From density measurements they deduced that there were 116 atoms in the unit cell and that the ideal formula was $\text{Pu}_{28}M$ (3.4 at.% M).

It recently became of interest to know the crystal structure of the phase and a serious effort was begun to determine the structure from the powder pattern. It has never been possible to prepare single crystals of this phase.

Structure determination

Considerable use was made of the program *GENLES*, the least-squares portion of the Los Alamos Crystal Structure codes developed primarily by A. C. Larson. One feature of this program is the ability to include

interatomic-distance constraints, *via* a potential function, and these interatomic distances become part of the observations along with the usual F_o . The two types of observation can be arbitrarily weighted, and in the extreme case the F_o can be omitted entirely and a trial structure refined with no experimental data whatsoever. Such a course was followed in the present investigation. Structures were generated, essentially at random, and refined to move the atoms apart to reasonable distances. First, the number of different atoms that could be accommodated in each of the various kinds of equipoints of a likely space group was determined. These were then combined in all possible ways to achieve a total of 116 atoms and then refined by *GENLES*. Physically possible models were then tested against the few known diffraction intensities given by ZE.

The correct space group, other than being body-centered tetragonal, was not evident from the lines indexed by ZE. In problems of this sort it is a reasonable strategy to start with the highest possible space group and, if no solution is found, to proceed to space groups of successively lower symmetry. $I4_1/acd$ could be eliminated because of the presence of an $h0l$ line with l odd. $I4_1/amd$ seemed likely because no $hk0$ lines with h and k odd were present and no hhl lines with $2h + l \neq 4n$ were evident. However, in the region indexed by ZE there was only one hhl line (442) of this class possible and this line was very close to 213. The initial assumption was made that 442 was absent and that the space group was $I4_1/amd$.

There are a large number of ways to distribute 116 atoms over the equipoints of $I4_1/amd$. Although many physically acceptable structures were generated, none fit the known intensities very well.

$I4/mmm$, the next lower symmetry space group which was possible, likewise provided many models with reasonable interatomic distances but none of these models gave acceptable calculated intensities.

A closer inspection of the actual pattern of ZE was then made. The 213 line, with perhaps a little imagination, was seen to be just slightly wider than resolved single lines on either side, suggesting that this line might indeed contain 442. If so, the space group could very well be $I4_1/a$, the next lower symmetry centrosymmetric space group.

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A new specimen was made by arc melting a 2.8 at.% Zr alloy followed by cold rolling and a heat treatment for one week at 473 K. The button was cut, imbedded in plastic and the flat surface was polished and chemically etched. The entire sample and mount were covered with a thin plastic sheet to reduce oxidation and to protect the apparatus from radioactive contamination. A diffractometer trace showed that the 213 line was a doublet and that 442 was indeed present.

Proceeding as above, a structure was soon found using the 4(*b*) position and seven 16-fold general positions of space group $I4_1/a$.

Refinement of the structure

Data for refinement were obtained with a Norelco diffractometer equipped with a Canberra 6511 operating system which makes possible automatic step scans with printing and punching of the counts at each step. A scan was made using Ni-filtered Cu $K\alpha$ radiation at steps of 0.01° from 30 to 125° 2θ with 10 s counts at each step. There are only a few weak lines below 30° and these are nearly obscured by scattering from the plastic wrap surrounding the sample.

Refinement was made by the pattern-fitting, structure-refinement (PFSR) technique using the program described by Young, Mackie & Von Dreele (1977). This program is a descendent of the original program and technique of Rietveld (1969). Refinement was made at 9501 points and in this 2θ range there were 2022 different hkl . About 90 s were required for each least-squares cycle on a CDC-7600. The original trial structure did not converge well and some inter-atomic distances were unreasonably small. The output atom positions from the PFSR program were recycled through GENLES which again moved the atoms apart. A slightly different model resulted which quickly converged with the PFSR program.

In addition to the usual scale-factor, positional and thermal parameters, the PFSR program can refine lattice parameters, line-shape parameters and the diffractometer 2θ zero-point. The line shape is represented by a Gaussian with full width at half height, H , given by

$$H^2 = U \tan^2 \theta + V \tan \theta + W.$$

In the present case we were unable to simultaneously refine U , V and W because of high correlation. W was therefore held constant at a value determined by an analysis of a pattern of MgO.

One other problem arose in the initial stages of refinement. The thermal parameters tended to be very small or negative. This problem was believed to be caused by absorption from a thin layer of PuO_2 on the specimen surface. The intensities were therefore correc-

ted for a thin absorbing layer by the function $I_{\text{corr}} = I_{\text{obs}} \exp(-\mu t \sec \theta)$ with $\mu t = 0.08$.

The final parameters are given in Table 1. The rather large value of the zero-point of 2θ arose because of a mechanical slippage in the early part of the step scan. Three other step scans were made but we were never able to prepare the specimen surface as well as was done the first time and thus were forced to use the pattern with the error in zero 2θ . The standard deviations given in Table 1 are those calculated by the PFSR program. These are gross underestimates, particularly those of the positional parameters. These parameters changed as much as 7σ as changes were made in the background. It was difficult to estimate the background with 2θ greater than 50° because of the large number of overlapping lines and the final estimate was of necessity rather arbitrary.

The PFSR program computes three R indices. These are

$$R_1 = 100 \sum_{hkl} \left| I(\text{obs.}) - \frac{1}{c} I(\text{calc.}) \right| / \sum I(\text{obs.}) = 17.1,$$

$$R_2 = 100 \sum \left| Y(\text{obs.}) - \frac{1}{c} y(\text{calc.}) \right| / \sum y(\text{obs.}) = 28.7,$$

$$R_3 = 100 \left\{ \sum w \left[y(\text{obs.}) - \frac{1}{c} y(\text{calc.}) \right]^2 / \sum w [y(\text{obs.})]^2 \right\}^{1/2} \\ = 22.8.$$

In the above, the $I(\text{obs.})$ are approximate values of observed $F^2(hkl)$ obtained from decomposing reflection profiles in the ratios of calculated $F^2(hkl)$, the $y(\text{obs.})$ and $y(\text{calc.})$ are observed and calculated intensities at each step in the profile, c is a scale factor and w is the weight of each point given by $w = 1/\sigma^2 = 1/y(\text{obs.})$ (Rietveld, 1969).

Table 1. Parameters for ζ -Pu-Zr obtained from the pattern-fitting structure-refinement program

The origin is at a center of symmetry.

	x	y	z
Pu(1)	0	$\frac{1}{4}$	$\frac{5}{8}$
Pu(2)	0.3434 (5)	0.1677 (5)	0.0101 (13)
Pu(3)	0.2119 (5)	0.2877 (5)	0.1203 (12)
Pu(4)	0.1175 (5)	0.1730 (5)	0.3848 (12)
Pu(5)	0.2480 (5)	0.4165 (6)	0.8391 (10)
Pu(6)	0.4501 (6)	0.1788 (6)	0.2358 (13)
Pu(7)	0.2015 (6)	0.0942 (6)	0.0576 (10)
Pu(8)	0.9761 (4)	0.5644 (5)	0.5093 (11)

$$B = 0.30 (3) \text{ \AA}^2 \\ \alpha = 18.1899 (3) \text{ \AA} \\ c = 7.8576 (2)$$

$$U = 264.4 (15.1) \text{ deg}^2 \\ V = -210.8 (9.4) \\ W = 195.3$$

$$Z(\text{zero-point}) = 0.125 (0.077)^\circ$$

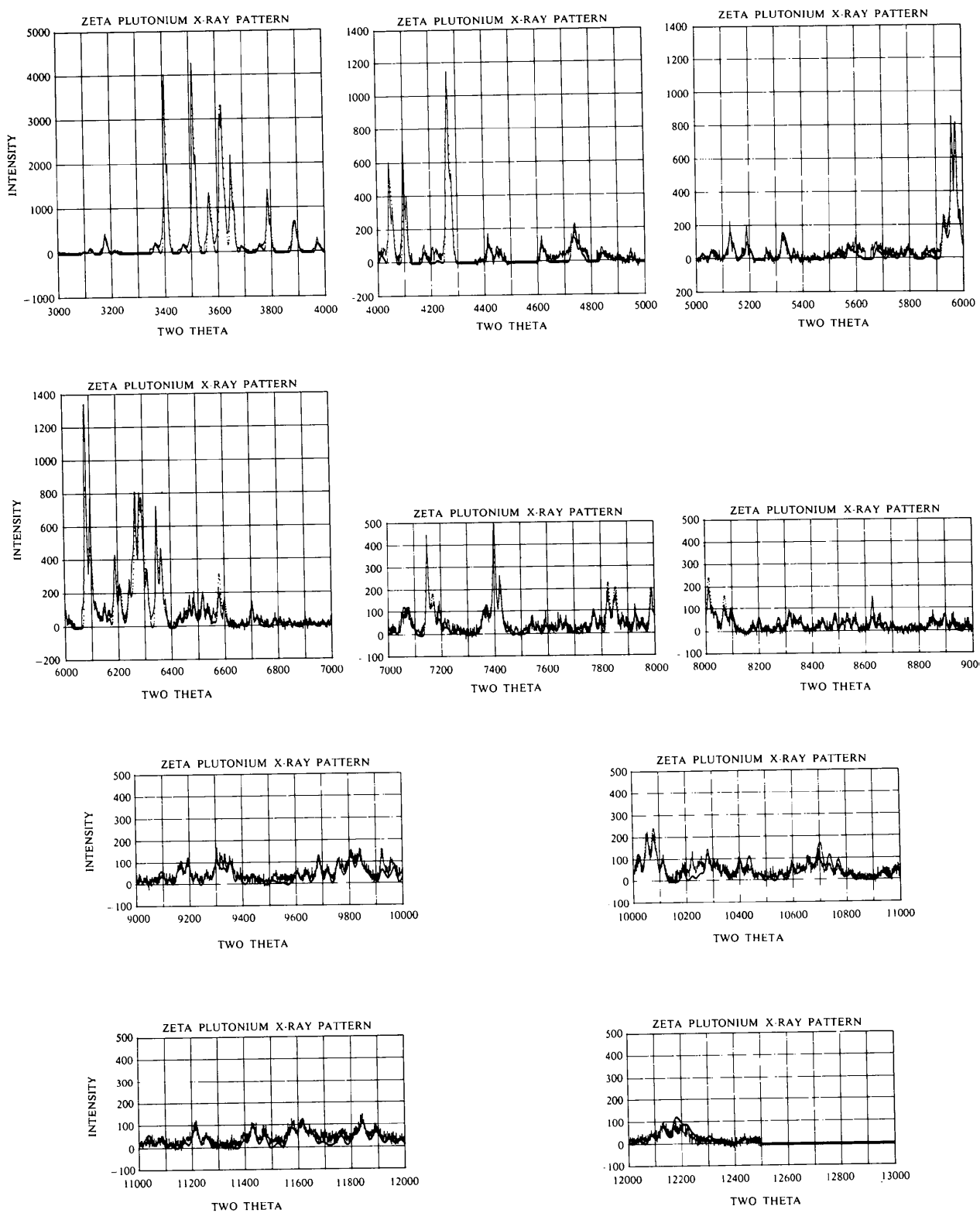


Fig. 1. Comparison of observed and calculated diffractometer patterns for ζ -Pu-Zr. The ordinate is actual counts and the abscissa is hundredths of a degree 2θ . The light solid line connects the observed points and the dots give the calculated values. In many places the dots merge together to give a heavy solid line.

Use of individual isotropic thermal parameters was attempted but the fit was not significantly improved. Pu scattering factors f , f' and f'' used for all atoms were taken from *International Tables for X-ray Crystallography* (1974).

The calculated and observed profiles are shown in Fig. 1. The fit is qualitatively good but many of the larger peak heights are calculated too low. This disagreement may be because the peak shape is not really Gaussian, although the examples shown by Young *et al.* (1977) do not show this discrepancy. Another possibility is that the specimen contained a small amount of α - and/or β -Pu. Many of the strong lines of α and β occur close to the strong lines of the present phase. Inclusion of other phases is quite possible in the *PFSR* method but was not believed worth doing in the present case.

Discussion

If the structure is ordered, the Zr atoms must be in the 4(b) equipoint and the ideal stoichiometry is Pu_{28}M as noted by ZE. It seems logical that with such a small amount of Zr present the phase would not form at all if it were not ordered. Indeed, other structures of high ratio, *e.g.* ReBe_{22} (Sands, Johnson, Zalkin, Krikorian & Kromholtz, 1962), are ordered. On the other hand, η - Pu_{19}Os (Cromer, 1978) cannot be fully ordered because there are 40 atoms in the unit cell in five eightfold sets. Similarly, in ζ - Pu_{19}Os (Cromer, 1979), a high-temperature phase of approximately the same composition, there are 52 atoms in five eightfold and three fourfold sets and this phase cannot be fully ordered either. A run with individual thermal parameters did not give an especially large value for atom (1) so there is no direct evidence for ordering. In addition, a calculation with a Zr scattering factor for atom (1) gave a strongly negative thermal parameter for this atom. Although the structure is probably ordered, the data are not good enough to directly show the ordering.

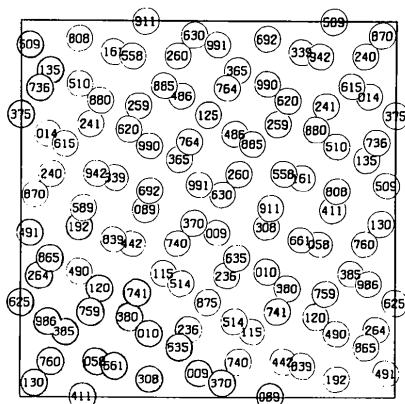


Fig. 2. The unit cell of ζ -Pu-Zr projected along the c axis. Each number inside a circle gives the z coordinate of the atom.

For discussion purposes all atoms are assumed to be Pu.

A drawing of the structure projected down the z axis is shown in Fig. 2 and interatomic distances are given in Table 2. Standard deviations for these distances were all about 0.010 to 0.015 Å but as noted earlier these are surely underestimated. A more reasonable value is about 0.04 Å.

Table 2. *Interatomic distances (Å) in ζ -Pu-Zr*

Standard deviations are estimated to be about 0.04 Å.

Pu(1)—4Pu(2)	3.39	Pu(5)—Pu(2)	3.19
4Pu(4)	3.18	Pu(2)	3.56
4Pu(6)	3.25	Pu(3)	3.29
4Pu(8)	3.57	Pu(4)	3.24
		Pu(4)	3.65
		2Pu(5)	2.91
		Pu(7)	3.19
		Pu(7)	3.26
		Pu(7)	3.31
		Pu(7)	3.44
		Pu(8)	2.96
		Pu(8)	3.70
Pu(2)—Pu(1)	3.39	Pu(6)—Pu(1)	3.25
Pu(3)	3.18	Pu(2)	2.64
Pu(3)	3.35	Pu(3)	3.20
Pu(4)	3.10	Pu(3)	3.22
Pu(4)	3.35	Pu(4)	3.11
Pu(5)	3.19	Pu(4)	3.19
Pu(5)	3.56	Pu(4)	3.28
Pu(6)	2.64	2Pu(6)	3.13
Pu(7)	2.93	Pu(6)	3.16
Pu(7)	3.19	Pu(7)	3.11
Pu(8)	2.91	Pu(8)	2.78
Pu(8)	3.06		
Pu(8)	3.64		
Pu(3)—Pu(2)	3.18	Pu(7)—Pu(2)	2.93
Pu(2)	3.35	Pu(2)	3.19
Pu(3)	2.82	Pu(3)	3.20
Pu(4)	3.18	Pu(3)	3.56
Pu(4)	3.41	Pu(3)	3.67
Pu(4)	3.49	Pu(4)	3.32
Pu(5)	3.29	Pu(5)	3.19
Pu(6)	3.20	Pu(5)	3.26
Pu(6)	3.22	Pu(5)	3.31
Pu(7)	3.20	Pu(5)	3.44
Pu(7)	3.56	Pu(6)	3.11
Pu(7)	3.67		
Pu(8)	3.09		
Pu(8)	3.53		
Pu(4)—Pu(1)	3.18	Pu(8)—Pu(1)	3.57
Pu(2)	3.10	Pu(2)	2.91
Pu(2)	3.35	Pu(2)	3.06
Pu(3)	3.18	Pu(2)	3.64
Pu(3)	3.41	Pu(3)	3.09
Pu(3)	3.49	Pu(3)	3.53
Pu(5)	3.24	Pu(4)	3.34
Pu(5)	3.65	Pu(4)	3.35
Pu(6)	3.11	Pu(5)	2.96
Pu(6)	3.19	Pu(5)	3.70
Pu(6)	3.28	Pu(6)	2.78
Pu(7)	3.32	Pu(7)	3.37
Pu(8)	3.34	Pu(8)	2.50
Pu(8)	3.35		

A relation between this structure and that of β -Pu was first sought because the X-ray patterns of the two are similar and the c axes are virtually the same. For β -Pu $c = 7.859 \text{ \AA}$ and the monoclinic body-centered cell with $\beta = 92.13^\circ$ is nearly orthogonal (Zachariasen & Ellinger, 1963a). A drawing of β -Pu projected along z was made and inspected for pseudo-fourfold symmetry but nothing very striking was evident. In the present ζ phase there is a rather short (2.50 \AA) distance for Pu(8)—Pu(8) through a center of symmetry. In β -Pu (Zachariasen & Ellinger, 1963a) the Pu(7)—Pu(7) distance through a center of symmetry is also short (2.59 \AA). If the two structures are superposed and oriented so that these two short distances are coincident there is a remarkable similarity between the two projected structures for a distance of several \AA about the short bonds. The coordination polyhedra about Pu(8) in ζ - and Pu(7) in β -Pu are also the same. No further structural similarities between the β and ζ phases could be found.

The neighbors and polyhedra were determined as described by Cromer & Larson (1977). The convex polyhedra are shown in Figs. 3–5. Pu(1) has 16 neighbors at distances ranging from 3.18 to 3.57 \AA . This atom is in a quite roomy cage and because a Zr atom is slightly larger than a Pu atom, this site is a likely place for the Zr atoms to order. The point symmetry is $\bar{4}$ which is the symmetry a Zr atom would have if in an sd^3 hybridized state. This polyhedron is the CN16 polyhedron described by Frank & Kasper (1958). Pu(2) and Pu(5) each have 13 neighbors at 2.64 to 3.64 \AA and 2.91 to 3.70 \AA respectively. Their polyhedra can be described as a ring of five atoms and a ring of six atoms on either side of the central atom with each ring capped by a single additional atom. Pu(4) and Pu(7) each have 14 neighbors arranged in two staggered rings of six atoms with each ring capped by a single atom; this is the Frank & Kasper CN14 polyhedron. The neighbors of Pu(4) range from 3.10 to 3.65 \AA and the Pu(7) neighbors range from 2.93 to

3.67 \AA . Pu(3) has 14 neighbors at 2.82 to 3.67 \AA . This polyhedron is difficult to describe. An approximate description is that it consists of a ring of five atoms on one side, capped by a single atom and a ring of six atoms on the other side, capped by two atoms. Pu(6) has 12 neighbors at 2.64 to 3.28 \AA making an irregular icosahedron. Pu(8) has 13 neighbors at distances from 2.50 to 3.70 \AA . There are five neighbors approximately coplanar with Pu(8) and four other neighbors on either side of this plane, although other descriptions are possible.

Zachariasen & Ellinger (1963a,b) discuss the structures of α - and β -Pu in terms of short and long bonds. In both cases the average number of short bonds is four. For ζ -Pu the division between short and long bonds is not well defined but if the dividing line is

Table 3. Distribution of short and long bonds and average bond lengths (\AA) in ζ -Pu-Zr

	Num- ber	Short bonds	Num- ber	Long bonds	Average bond
Pu(1)	0		16	3.18–3.57	3.344
Pu(2)	5	2.64–3.10	7	3.18–3.64	3.191
Pu(3)	2	2.82–3.09	12	3.18–3.67	3.298
Pu(4)	1	3.10	13	3.18–3.65	3.299
Pu(5)	3	2.91–2.96	10	3.19–3.70	3.277
Pu(6)	2	2.64–2.78	10	3.11–3.28	3.098
Pu(7)	1	2.93	13	3.11–3.67	3.304
Pu(8)	6	2.50–3.09	7	3.34–3.70	3.215

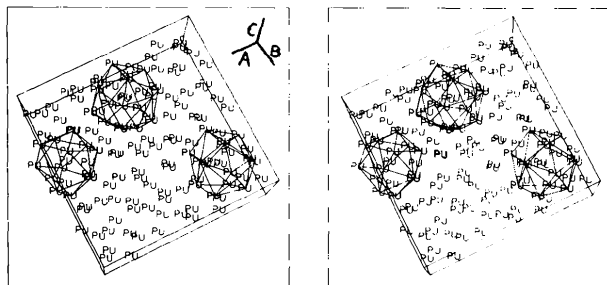


Fig. 3. Stereodrawing of the unit cell of ζ -Pu-Zr showing the polyhedra of Pu(1), Pu(2) and Pu(3). The direction of view is approximately along z and the origin is at the top rear where unit vectors A , B and C are drawn. The Pu(1) polyhedron is at the top at $(\frac{1}{2}, \frac{1}{2}, \frac{7}{8})$; the Pu(2) polyhedron is at the left at (0.918, 0.407, 0.760); the Pu(3) polyhedron is at the right at (0.212, 0.788, 0.880).

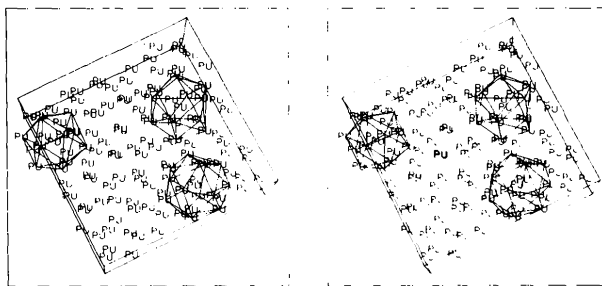


Fig. 4. As Fig. 3 but showing Pu(4) at the lower right at (0.382, 0.827, 0.885). Pu(5) is at the upper right at (0.248, 0.417, 0.839) and Pu(6) is at the left at (0.929, 0.300, 0.986).

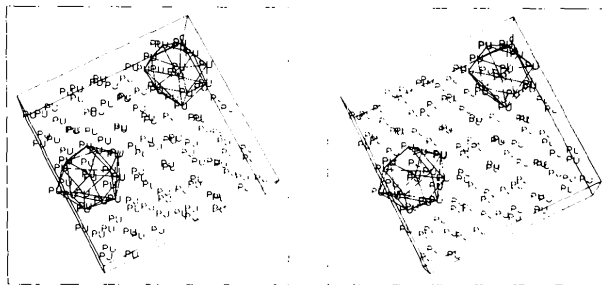


Fig. 5. As Fig. 3 but showing Pu(7) at the left at (0.844, 0.549, 0.808) and Pu(8) at the right at (0.186, 0.226, 0.759).

made between 3.10 and 3.11 Å (as was done for β -Pu) the results are as shown in Table 3. Disregarding Pu(1), which is probably Zr, the average number of short bonds is three.

Zachariassen (1973) has discussed the radii of Pu and other actinide elements in their various phases and deduced the number of valence electrons. He defines the radius as $r = V_a^{1/3}/2^{5/6}$ where V_a is the mean atomic volume. For the present material $V_a = 22.42 \text{ \AA}^3$, $r = 1.583 \text{ \AA}$ and the mean valence is therefore 5.2 electrons. This value is the same as that of γ -Pu.

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Hydrogen Bonds in Schlippe's Salt: Refinement of the Crystal Structures of $\text{Na}_3\text{SbS}_4 \cdot 9\text{H}_2\text{O}$ by X-ray Diffraction and $\text{Na}_3\text{SbS}_4 \cdot 9\text{D}_2\text{O}$ by Neutron Diffraction at Room Temperature

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Abstract

The room-temperature crystal structure of Schlippe's salt, space group $P2_13$, $Z = 4$, has been refined for $\text{Na}_3\text{SbS}_4 \cdot 9\text{H}_2\text{O}$, $a = 11.957(3) \text{ \AA}$, from X-ray data to $R_F = 0.022$, and for $\text{Na}_3\text{SbS}_4 \cdot 9\text{D}_2\text{O}$, $a = 11.959(3) \text{ \AA}$, from neutron data to $R_F = 0.058$. X-ray and neutron results are in good agreement. Within experimental error, no structural isotope effect between the H and D compounds is observed. Finite groups of

distorted, face-sharing Na coordination octahedra, $[(\text{H}_2\text{O})_3\text{Na}(\text{H}_2\text{O})_3\text{Na}(\text{H}_2\text{O})_3\text{NaS}_3]$ (point symmetry 3), and SbS_4 tetrahedra (point symmetry 3) share common corners *via* three of their four S atoms to form a three-dimensional framework. Average bond lengths are $\text{Na}-\text{O} = 2.39$, $\text{Na}-\text{S} = 3.00$, $\text{Sb}-\text{S} = 2.33 \text{ \AA}$. D_2O molecules with $\text{D}-\text{O} = 0.93-0.97 \text{ \AA}$ and $\text{D}-\text{O}-\text{D} = 107-108^\circ$ form an extensive hydrogen-bond system. Six different bonds are observed: one $\text{O}-\text{D}\cdots\text{O}$ ($\text{O}\cdots\text{O} = 2.81 \text{ \AA}$), four approximately linear