

Table 1 are not directly accessible. The x and y coordinates were obtained through a least-squares refinement to a final reliability index of $R=0.084$ by Herpin & Meriel (1964) indicating that the estimated standard deviation in these coordinates should be about 0.01 \AA . The z coordinate of the H atom is also determined with the same accuracy as outlined above. The uncertainties in the z coordinates of the heavy atoms, however, are probably larger than this as they have been obtained directly from the (001) electron density projection (Herpin, 1952). However, the coordinates in Table 1 seem to give a very consistent picture of the structure of the $(\text{HCO}_3)_2^-$ ion as apparent from inspection of Fig. 1 and Fig. 3, indicating that the given atomic positions are accurate to about 0.01 \AA .

References

- BACON, G. E. & CURRY, N. A. (1956). *Acta Cryst.* **9**, 82.
 HAMILTON, W. C. (1962). *Ann. Rev. Phys. Chem.* **13**, 19.
 HERPIN, P. (1952). *C. r. Acad. Sci. Paris*, **234**, 2205.
 HERPIN, P. & MERIEL, P. (1964). *J. Phys.* **25**, 484.
 KUME, K. & KAKIUCHI, Y. (1960). *J. Phys. Soc. Japan*, **15**, 1277.
 NITTA, I., TOMIIE, Y. & KOO, C. H. (1952). *Acta Cryst.* **5**, 292.
 NITTA, I., TOMIIE, Y. & KOO, C. H. (1954). *Acta Cryst.* **7**, 140.
 PEDERSEN, B. (1968). *Acta Chem. Scand.* To be published.
 PEDERSEN, B. F. & PEDERSEN, B. (1967). *Selected Topics in Structure Chemistry*, p. 253. Oslo Univ. Press.
 ROBERTSON, J. H. (1964). *Acta Cryst.* **17**, 316.
 SASS, R. L. & SCHEUERMAN, R. F. (1962). *Acta Cryst.* **15**, 77.

Acta Cryst. (1968). **B24**, 480

The Crystal Structure of $\text{Pu}_3\text{Zn}_{22}$

BY QUINTIN JOHNSON, DAVID H. WOOD AND GORDON S. SMITH

Lawrence Radiation Laboratory, University of California, Livermore, California, U.S.A.

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The structure of a compound present in the Pu–Zn system at the approximate stoichiometry $\text{PuZn}_{7.7}$ has been determined from diffractometrically recorded, single-crystal intensities. The unit cell, containing four formula units of $\text{Pu}_3\text{Zn}_{22}$, is body-centered tetragonal with $a=8.85$, $c=21.18 \text{ \AA}$. The calculated density is 8.71 g.cm^{-3} , and the space group is $I4_1/amd$. This structure also accounts for the published powder pattern of a compound in the Ce–Zn system. Cell constants for $\text{Ce}_3\text{Zn}_{22}$ are $a=8.930$, $c=21.36 \text{ \AA}$.

Introduction

A compound with the approximate composition $\text{PuZn}_{7.7}$ was discovered in a phase-relation study of the zinc-rich region of the Pu–Zn system (Cramer & Wood, 1967). The composition and symmetry indicated this to be a new structure type; we have carried out a determination of this structure to establish the actual composition of this material.

Experimental

Details concerning the preparation of $\text{Pu}_3\text{Zn}_{22}$ are given by Cramer & Wood (1967). To minimize accidental contamination as well as to protect from the atmosphere, crystals were coated with Canada balsam dissolved in xylene. This procedure proved to be more convenient than the use of capillaries, yet provided adequate protection from the radioactive hazards of plutonium.

Single-crystal oscillation, Weissenberg and precession photos showed tetragonal symmetry. The systematic extinctions [$h+k+l \neq 2n$; $hk0: h, (k) \neq 2n$; $hhl: (l \neq 2n)$; $2h+l \neq 4n$] and the $4/mmm$ Laue symmetry uniquely characterize the space group $I4_1/amd$. Lattice

constants, $a=8.85$ and $c=21.18 \text{ \AA}$, were obtained from uncalibrated Weissenberg and precession photographs and are thought to be accurate to about 0.3% .

Intensities were recorded diffractometrically with use of zirconium filtered Mo $K\alpha$ radiation ($\lambda=0.7107 \text{ \AA}$). A total of 229 independent reflections were measured up to a 2θ value of 40° . The shape of the crystal resembled a distorted cylinder. A 2θ -dependent absorption correction was applied assuming a cylindrical shape ($\mu r=3.0$). In addition, a pronounced dependence of intensity with respect to φ was observed. An attempt to remove this dependency was made by measuring the intensities of several reflections at $\chi=90^\circ$ as a function of φ and applying the indicated correction to all data dependent only on the φ value at which the reflection was observed. This correction, which amounted to $\pm 50\%$, was modified in the course of refinements as will be discussed later.

Determination of the structure

Precession photos of $\text{Pu}_3\text{Zn}_{22}$ were quite similar to those of the $\text{Th}_2\text{Ni}_{17}$ - and $\text{Th}_2\text{Zn}_{17}$ -like compounds of Pu–Zn. For example, the $hk0$ zone of $\text{Pu}_3\text{Zn}_{22}$ could be mistaken for the hhl zone of $\text{Pu}_2\text{Zn}_{17}$ ($\text{Th}_2\text{Ni}_{17}$ -like).

Table 1. *Final parameters*
e.s.d.'s are given in parentheses.

| | Wyckoff notation* | 10 ⁴ x | 10 ⁴ y | 10 ⁴ z | B |
|--------|-------------------|-------------------|-------------------|-------------------|----------------------------|
| Pu (1) | 8(e) | 0 | 0 | 1217 (3) | 1·20 (0·14) Å ² |
| Pu (2) | 4(b) | 0 | 0 | 1/2 | 1·19 (0·19) |
| Zn (1) | 32(i) | 2413 (13) | 2309 (11) | 1853 (4) | 2·13 (0·17) |
| Zn (2) | 8(d) | 0 | 1/4 | 5/8 | 1·58 (0·37) |
| Zn (3) | 16(h) | 0 | 2204 (15) | 18 (7) | 2·16 (0·30) |
| Zn (4) | 16(h) | 0 | 1475 (15) | 7415 (6) | 2·15 (0·29) |
| Zn (5) | 16(h) | 0 | 1526 (16) | 3625 (6) | 2·06 (0·29) |

* Space group *I*₄₁/*amd* with origin at $\bar{4}m2$.

Table 2. *Observed and calculated structure factors and the phase angle, α*

Phase angles differ from the expected values for a centrosymmetric structure because anomalous dispersion corrections have been made.

| H | K | L | F _o | F _c | ALPHA | H | K | L | F _o | F _c | ALPHA | H | K | L | F _o | F _c | ALPHA | H | K | L | F _o | F _c | ALPHA | H | K | L | F _o | F _c | ALPHA | H | K | L | F _o | F _c | ALPHA | H | K | L | F _o | F _c | ALPHA | | | | | | |
|---|---|----|----------------|----------------|-------|---|---|----|----------------|----------------|-------|---|----|-----|----------------|----------------|-------|---|---|----|----------------|----------------|-------|---|---|-----|----------------|----------------|-------|---|----|-----|----------------|----------------|-------|---|----|-----|----------------|----------------|-------|---|---|-----|-----|-------|-------|
| 0 | 0 | 4 | 64 | 67 | 183.2 | 2 | 0 | 18 | 108 | 103 | 95.2 | 3 | 1 | 8 | 117 | 117 | 273.9 | 4 | 1 | 1 | 98 | 85 | 318.7 | 4 | 4 | 12 | 46 | 58 | 184.7 | 5 | 3 | 10 | 192 | 235 | 4.8 | 6 | 2 | 2 | 95 | 78 | 94.6 | 7 | 1 | 4 | 0 | 2 | 95.0 |
| 0 | 0 | 8 | 622 | 846 | 3.5 | 2 | 1 | 58 | 44 | 318.3 | 3 | 1 | 10 | 175 | 173 | 4.0 | 4 | 1 | 3 | 28 | 21 | 226.6 | 5 | 0 | 1 | 37 | 39 | 49.0 | 5 | 3 | 12 | 28 | 24 | 275.2 | 6 | 2 | 4 | 127 | 126 | 184.5 | 7 | 1 | 6 | 16 | 16 | 186.4 | |
| 0 | 0 | 12 | 66 | 39 | 4.2 | 2 | 1 | 3 | 234 | 206 | 428.3 | 3 | 1 | 12 | 28 | 27 | 94.4 | 4 | 1 | 5 | 58 | 39 | 319.1 | 5 | 3 | 162 | 173 | 139.3 | 5 | 3 | 14 | 60 | 55 | 5.2 | 6 | 2 | 6 | 72 | 66 | 274.8 | 7 | 1 | 8 | 0 | 20 | 95.2 | |
| 0 | 0 | 16 | 762 | 772 | 4.6 | 2 | 1 | 5 | 299 | 271 | 138.4 | 3 | 1 | 14 | 18 | 20 | 4.3 | 4 | 1 | 7 | 79 | 83 | 49.0 | 5 | 5 | 5 | 73 | 74 | 229.0 | 5 | 4 | 1 | 100 | 90 | 49.5 | 6 | 2 | 8 | 57 | 18 | 1.1 | 7 | 1 | 10 | 34 | 24 | 187.5 |
| 0 | 0 | 20 | 81 | 38 | 184.7 | 2 | 1 | 7 | 52 | 53 | 48.6 | 3 | 1 | 16 | 139 | 122 | 275.0 | 4 | 1 | 9 | 62 | 61 | 319.2 | 5 | 0 | 7 | 34 | 4 | 139.7 | 5 | 4 | 3 | 108 | 117 | 139.4 | 6 | 2 | 10 | 17 | 1 | 95.1 | 7 | 2 | 1 | 17 | 9 | 230.9 |
| 1 | 0 | 1 | 15 | 4 | 227.3 | 2 | 1 | 9 | 41 | 36 | 318.8 | 3 | 1 | 18 | 165 | 149 | 5.0 | 4 | 1 | 11 | 26 | 31 | 228.8 | 5 | 0 | 9 | 54 | 55 | 49.4 | 5 | 4 | 5 | 49 | 42 | 53.6 | 6 | 2 | 12 | 64 | 59 | 184.8 | 7 | 2 | 3 | 227 | 229 | 139.8 |
| 1 | 0 | 3 | 81 | 57 | 139.3 | 2 | 1 | 11 | 204 | 201 | 229.5 | 3 | 2 | 1 | 53 | 45 | 48.6 | 4 | 1 | 13 | 40 | 28 | 134.3 | 5 | 0 | 11 | 67 | 57 | 326.4 | 5 | 4 | 7 | 73 | 77 | 319.8 | 6 | 3 | 1 | 19 | 13 | 314.3 | 7 | 2 | 5 | 60 | 86 | 229.5 |
| 1 | 0 | 5 | 170 | 147 | 228.1 | 2 | 1 | 13 | 214 | 203 | 139.2 | 3 | 2 | 3 | 558 | 563 | 138.6 | 4 | 1 | 15 | 53 | 45 | 50.1 | 5 | 0 | 13 | 229 | 228 | 229.8 | 5 | 4 | 9 | 56 | 67 | 49.9 | 6 | 3 | 3 | 374 | 363 | 229.7 | 7 | 2 | 7 | 0 | 3 | 142.6 |
| 1 | 0 | 7 | 51 | 35 | 138.4 | 2 | 1 | 15 | 51 | 44 | 49.7 | 3 | 2 | 5 | 371 | 380 | 224.7 | 4 | 1 | 17 | 56 | 48 | 320.0 | 5 | 0 | 15 | 37 | 28 | 140.3 | 5 | 4 | 11 | 23 | 15 | 137.3 | 6 | 3 | 5 | 303 | 314 | 139.7 | 7 | 2 | 9 | 17 | 23 | 231.1 |
| 1 | 0 | 9 | 55 | 41 | 48.6 | 2 | 1 | 17 | 36 | 28 | 319.5 | 3 | 2 | 7 | 0 | 3 | 318.7 | 4 | 2 | 0 | 177 | 118 | 183.9 | 5 | 1 | 2 | 169 | 144 | 4.0 | 5 | 4 | 13 | 46 | 70 | 229.5 | 6 | 3 | 7 | 35 | 28 | 230.1 | 7 | 3 | 2 | 18 | 6 | 359.9 |
| 1 | 0 | 11 | 74 | 63 | 319.3 | 2 | 1 | 19 | 116 | 116 | 236.1 | 3 | 2 | 9 | 43 | 42 | 49.0 | 4 | 2 | 2 | 2137 | 122 | 273.9 | 5 | 1 | 4 | 0 | 2 | 274.2 | 5 | 5 | 2 | 156 | 164 | 4.7 | 6 | 3 | 9 | 40 | 45 | 319.9 | 7 | 3 | 4 | 8 | 275.2 | |
| 1 | 0 | 13 | 291 | 219 | 229.1 | 2 | 2 | 0 | 270 | 412 | 3.4 | 3 | 2 | 11 | 338 | 317 | 139.3 | 4 | 2 | 4 | 131 | 121 | 183.9 | 5 | 1 | 6 | 142 | 140 | 4.2 | 5 | 5 | 6 | 147 | 173 | 5.0 | 6 | 3 | 11 | 160 | 182 | 230.1 | 7 | 3 | 6 | 0 | 11 | 3.1 |
| 1 | 0 | 15 | 56 | 29 | 139.5 | 2 | 2 | 4 | 225 | 228 | 183.5 | 3 | 2 | 13 | 355 | 325 | 229.5 | 4 | 2 | 6 | 133 | 103 | 94.1 | 5 | 1 | 8 | 42 | 39 | 274.4 | 5 | 5 | 0 | 156 | 191 | 5.2 | 6 | 4 | 0 | 132 | 125 | 4.4 | 7 | 3 | 8 | 69 | 78 | 95.5 |
| 1 | 0 | 17 | 73 | 53 | 49.7 | 2 | 2 | 8 | 281 | 263 | 183.8 | 3 | 2 | 15 | 49 | 45 | 139.9 | 4 | 2 | 8 | 431 | 427 | 4.2 | 5 | 1 | 10 | 132 | 144 | 4.5 | 6 | 6 | 0 | 413 | 360 | 4.3 | 6 | 4 | 2 | 127 | 121 | 95.0 | 7 | 4 | 1 | 17 | 5 | 445.1 |
| 1 | 0 | 19 | 34 | 22 | 322.2 | 2 | 2 | 12 | 130 | 113 | 184.2 | 3 | 2 | 17 | 43 | 46 | 49.9 | 4 | 2 | 10 | 80 | 72 | 274.4 | 5 | 1 | 12 | 15 | 4 | 274.9 | 6 | 0 | 2 | 42 | 44 | 94.4 | 6 | 4 | 6 | 66 | 73 | 184.7 | 7 | 4 | 3 | 58 | 34 | 322.1 |
| 1 | 1 | 2 | 69 | 59 | 3.3 | 2 | 2 | 16 | 275 | 271 | 4.7 | 3 | 3 | 2 | 256 | 214 | 3.8 | 4 | 2 | 12 | 144 | 140 | 184.6 | 5 | 1 | 14 | 86 | 85 | 5.1 | 6 | 0 | 4 | 94 | 60 | 184.3 | 6 | 4 | 6 | 127 | 145 | 275.2 | 7 | 4 | 5 | 74 | 90 | 229.8 |
| 1 | 1 | 4 | 82 | 87 | 34.4 | 3 | 0 | 1 | 15 | 7 | 228.2 | 3 | 3 | 6 | 98 | 90 | 3.9 | 4 | 2 | 14 | 74 | 73 | 95.0 | 5 | 1 | 16 | 40 | 43 | 275.5 | 6 | 0 | 6 | 69 | 59 | 274.6 | 6 | 4 | 8 | 361 | 389 | 5.1 | 8 | 0 | 573 | 574 | 5.2 | |
| 1 | 1 | 10 | 56 | 57 | 3.7 | 3 | 0 | 3 | 281 | 275 | 138.5 | 3 | 3 | 10 | 228 | 278 | 4.3 | 4 | 2 | 16 | 22 | 27 | 1.8 | 5 | 2 | 1 | 66 | 62 | 49.1 | 6 | 0 | 8 | 605 | 655 | 4.7 | 6 | 4 | 10 | 70 | 72 | 95.5 | 8 | 0 | 2 | 0 | 11 | 275.6 |
| 1 | 1 | 14 | 75 | 76 | 4.3 | 3 | 0 | 5 | 469 | 466 | 226.6 | 3 | 3 | 14 | 33 | 42 | 185.2 | 4 | 3 | 1 | 80 | 76 | 319.7 | 5 | 2 | 3 | 138 | 129 | 139.1 | 6 | 0 | 10 | 84 | 79 | 95.0 | 6 | 5 | 1 | 32 | 35 | 320.0 | 8 | 0 | 4 | 53 | 77 | 185.0 |
| 1 | 1 | 18 | 79 | 78 | 4.5 | 3 | 0 | 7 | 83 | 88 | 138.7 | 4 | 0 | 0 | 897 | 931 | 3.7 | 4 | 3 | 3 | 196 | 189 | 229.0 | 5 | 2 | 5 | 296 | 291 | 229.2 | 6 | 0 | 12 | 52 | 65 | 184.8 | 6 | 5 | 3 | 92 | 106 | 229.8 | 8 | 0 | 6 | 51 | 56 | 95.6 |
| 2 | 0 | 0 | 265 | 199 | 3.3 | 3 | 0 | 9 | 69 | 70 | 48.9 | 4 | 0 | 2 | 109 | 121 | 273.7 | 4 | 3 | 5 | 236 | 225 | 139.1 | 5 | 2 | 7 | 51 | 52 | 319.4 | 6 | 0 | 14 | 15 | 18 | 275.5 | 6 | 5 | 5 | 219 | 247 | 140.1 | 8 | 1 | 0 | 12 | 161.2 | |
| 2 | 0 | 2 | 28 | 18 | 273.2 | 3 | 0 | 11 | 272 | 231 | 139.1 | 4 | 0 | 4 | 80 | 90 | 183.8 | 4 | 3 | 7 | 37 | 27 | 49.3 | 5 | 2 | 9 | 71 | 72 | 49.5 | 6 | 1 | 1 | 14 | 13 | 319.1 | 6 | 5 | 7 | 14 | 4 | 49.4 | 8 | 1 | 3 | 56 | 73 | 229.7 |
| 2 | 0 | 4 | 122 | 111 | 183.3 | 3 | 0 | 13 | 287 | 237 | 229.4 | 4 | 0 | 6 | 172 | 178 | 93.9 | 4 | 3 | 9 | 72 | 80 | 319.4 | 5 | 2 | 11 | 239 | 233 | 139.7 | 6 | 1 | 3 | 151 | 145 | 229.3 | 6 | 6 | 0 | 386 | 365 | 5.3 | 8 | 1 | 5 | 70 | 85 | 139.7 |
| 2 | 0 | 6 | 65 | 65 | 93.5 | 3 | 0 | 15 | 121 | 98 | 139.8 | 4 | 0 | 8 | 302 | 296 | 4.0 | 4 | 3 | 11 | 233 | 254 | 229.8 | 5 | 2 | 13 | 113 | 118 | 229.7 | 6 | 1 | 5 | 248 | 243 | 139.5 | 7 | 0 | 1 | 48 | 53 | 230.0 | 8 | 2 | 0 | 59 | 82 | 4.2 |
| 2 | 0 | 8 | 777 | 842 | 3.6 | 3 | 0 | 17 | 58 | 53 | 49.9 | 4 | 0 | 10 | 41 | 28 | 274.5 | 4 | 3 | 13 | 66 | 50 | 139.0 | 5 | 2 | 15 | 31 | 39 | 320.5 | 6 | 1 | 7 | 11 | 5 | 230.2 | 7 | 0 | 3 | 46 | 32 | 321.1 | 8 | 2 | 2 | 39 | 46 | 275.3 |
| 2 | 0 | 10 | 77 | 77 | 93.9 | 3 | 0 | 19 | 38 | 30 | 139.0 | 4 | 0 | 12 | 10 | 21 | 183.6 | 4 | 3 | 15 | 17 | 16 | 335.2 | 5 | 3 | 2 | 229 | 220 | 4.3 | 6 | 1 | 9 | 26 | 38 | 319.6 | 7 | 0 | 7 | 60 | 58 | 146.2 | 8 | 2 | 4 | 83 | 91 | 185.1 |
| 2 | 0 | 12 | 130 | 132 | 184.1 | 3 | 1 | 2 | 253 | 181 | 3.5 | 4 | 0 | 14 | 111 | 104 | 94.9 | 4 | 4 | 0 | 942 | 507 | 4.2 | 5 | 3 | 4 | 20 | 12 | 274.4 | 6 | 1 | 11 | 85 | 97 | 229.7 | 7 | 0 | 9 | 0 | 4 | 46.3 | | | | | | |
| 2 | 0 | 14 | 51 | 45 | 94.5 | 3 | 1 | 4 | 22 | 17 | 94.6 | 4 | 0 | 16 | 598 | 536 | 5.1 | 4 | 4 | 8 | 102 | 184.2 | 5 | 3 | 6 | 107 | 107 | 4.4 | 6 | 1 | 13 | 208 | 224 | 140.1 | 7 | 0 | 11 | 78 | 77 | 139.8 | | | | | | | |
| 2 | 0 | 16 | 108 | 104 | 4.2 | 3 | 1 | 6 | 85 | 75 | 3.7 | 4 | 0 | 18 | 59 | 59 | 95.6 | 4 | 4 | 8 | 65 | 79 | 4.0 | 5 | 3 | 8 | 51 | 47 | 94.7 | 6 | 2 | 0 | 435 | 411 | 4.4 | 7 | 1 | 2 | 45 | 27 | 185.8 | | | | | | |

Table 3. *Interatomic distances in Pu₃Zn₂₂*

| | Ligancy | Distance | | Ligancy | Distance | |
|----------|----------|----------|----------|----------|----------|-------|
| Pu (1) | 2 Zn (5) | 3·070 Å | Zn (3) | 2 Zn (1) | 2·549 Å | |
| | 2 Zn (4) | 3·180 | | 1 Zn (5) | 2·670 | |
| | 2 Zn (3) | 3·202 | | 2 Zn (3) | 2·751 | |
| | 4 Zn (1) | 3·240 | | 2 Zn (1) | 2·767 | |
| | 2 Zn (3) | 3·262 | | 2 Zn (4) | 2·797 | |
| | 4 Zn (1) | 3·410 | | 1 Pu (1) | 3·202 | |
| Pu (2) | 2 Zn (2) | 3·644 | 1 Pu (1) | 3·262 | | |
| | 4 Zn (4) | 3·114 | 1 Pu (1) | 3·644 | | |
| | 4 Zn (5) | 3·212 | Zn (4) | 1 Zn (2) | 2·603 | |
| | 8 Zn (1) | 3·352 | | 1 Zn (4) | 2·631 | |
| | 4 Zn (2) | 3·448 | | 2 Zn (1) | 2·691 | |
| | Zn (1) | 1 Zn (3) | | 2·549 | 2 Zn (1) | 2·788 |
| | | 1 Zn (1) | | 2·581 | 2 Zn (3) | 2·797 |
| | | 1 Zn (2) | | 2·621 | 2 Zn (5) | 2·894 |
| | | 1 Zn (4) | 2·691 | 1 Pu (2) | 3·114 | |
| | 1 Zn (5) | 2·721 | 1 Pu (1) | 3·180 | | |
| 1 Zn (5) | 2·746 | 1 Zn (5) | 3·563 | | | |
| 1 Zn (1) | 2·766 | Zn (5) | 2 Zn (2) | 2·597 | | |
| 1 Zn (3) | 2·767 | | 1 Zn (3) | 2·670 | | |
| 1 Zn (4) | 2·788 | | 2 Zn (1) | 2·693 | | |
| 1 Pu (1) | | | | | | |

The cell constants of Pu₃Zn₂₂ are related to Th₂Ni₁₇-like Pu₂Zn₁₇ as follows: $a_t \sim c_h$, $c_t \sim 4\sqrt{3}a_h$ where the subscripts refer to the tetragonal (Pu₃Zn₂₂) and hexagonal (Pu₂Zn₁₇) phases. This similarity proved to be more of a hindrance than a help since the structure is not as closely related to the Th₂Ni₁₇ structure as some of the special zonal photographs would indicate.

The structure was solved by recourse to a Patterson map to locate the 12 plutonium atoms. Difference Fourier calculations based on the contribution of plutonium atoms enabled us to locate 88 zinc atoms distributed among five different crystallographic sites. Full-matrix least-squares calculations, using isotropic thermal parameters and the scattering factors of Cromer & Waber (1965) corrected for anomalous dispersion (Cromer, 1965), resulted in an R value of 15%. The refinement was based on $|F|$ with the following weighting scheme (Smith, Johnson & Nordine, 1965): $w = F_o^{1/4}$, $F_o < A$; $w = A^{5/4}F_o^{-1}$, $F_o > A$, with $A = 510$.

The agreement was not appreciably affected when the experimentally measured, φ -dependent absorption correction was omitted. In this case, however, the ratio $(kF_o/F_c)^2$, when plotted as a function of φ , described a curve very similar to the experimentally measured φ -dependent absorption curve. This new curve was shifted by about 20° in φ . In subsequent and final refinements we used the measured φ curve shifted by 20°. This single change reduced the R factor to 9.6%. Parameters remained very nearly the same. The shift of the φ -curve probably in some way compensates for the lack of an explicit χ -dependency in the absorption correction.

No noticeable improvement was noted when plutonium atoms were described with anisotropic thermal parameters. Including a separate isotropic thermal parameter for each atom, the R value for 229 reflections is equal to 9.6%. Final atom parameters are shown in Table 1. Observed and calculated structure factors are presented in Table 2, and interatomic distances in

Table 4. Calculated and observed powder pattern for Ce₃Zn₂₂

(Observed data from Lott & Chiotti, 1966)

| h | k | l | d_o | d_c | I_o | I_c |
|-----|-----|-----|-------|-------|-------|-------|
| 1 | 0 | 1 | 8.246 | 8.239 | 1 | 1 |
| 1 | 0 | 3 | 5.569 | 5.567 | 1 | <1 |
| 1 | 1 | 2 | 5.443 | 5.436 | <1 | <1 |
| 0 | 0 | 4 | — | 5.340 | — | <1 |
| 2 | 0 | 0 | 4.467 | 4.465 | 2 | 1 |
| — | — | — | 4.276 | — | <1 | — |
| 2 | 0 | 2 | — | 4.119 | — | <1 |
| 2 | 1 | 1 | 3.929 | 3.926 | <1 | 1 |
| 1 | 0 | 5 | 3.855 | 3.854 | 2 | 2 |
| 2 | 1 | 3 | 3.483 | 3.483 | 15 | 15 |
| 2 | 0 | 4 | 3.428 | 3.425 | 2 | 2 |
| 2 | 2 | 0 | 3.156 | 3.157 | 23 | 15 |
| 1 | 1 | 6 | 3.104 | 3.101 | <1 | <1 |
| 3 | 0 | 1 | — | 2.948 | — | <1 |
| 2 | 1 | 5 | 2.916 | 2.917 | 23 | 24 |
| 1 | 0 | 7 | — | 2.888 | — | <1 |
| 2 | 0 | 6 | 2.783 | 2.784 | 1 | 1 |
| 3 | 0 | 3 | 2.745 | 2.746 | — | 11 |
| 3 | 1 | 2 | 2.730 | 2.730 | — | 8 |
| — | — | — | 2.725 | — | 28 | — |
| 2 | 2 | 4 | 2.718 | 2.718 | — | 10 |
| — | — | — | 2.704 | — | — | — |
| 0 | 0 | 8 | 2.670 | 2.670 | 10 | 18 |
| 3 | 1 | 4 | — | 2.496 | — | <1 |
| 3 | 2 | 1 | — | 2.460 | — | <1 |
| 3 | 0 | 5 | 2.442 | 2.442 | 28 | 35 |
| 2 | 1 | 7 | — | 2.425 | — | <1 |
| 3 | 2 | 3 | 2.339 | 2.339 | 87 | 101 |
| 1 | 0 | 9 | — | 2.294 | — | <1 |
| 2 | 0 | 8 | 2.292 | 2.292 | 100 | 100 |
| 4 | 0 | 0 | 2.232 | 2.233 | 43 | 66 |
| 3 | 1 | 6 | — | 2.212 | — | <1 |
| 4 | 0 | 2 | 2.185 | 2.185 | 2 | 2 |
| 4 | 1 | 1 | 2.154 | 2.155 | — | 2 |
| 3 | 2 | 5 | 2.142 | 2.143 | 31 | 30 |
| 3 | 0 | 7 | — | 2.131 | — | 1 |
| 4 | 1 | 3 | — | 2.072 | — | <1 |
| 3 | 3 | 2 | 2.065 | 2.065 | 9 | 4 |
| 4 | 0 | 4 | 2.054 | 2.060 | — | <1 |
| 2 | 1 | 9 | — | 2.040 | — | <1 |
| 2 | 2 | 8 | 2.039 | 2.039 | 25 | 22 |
| 1 | 1 | 10 | — | 2.023 | — | <1 |
| 4 | 2 | 0 | 1.997 | 1.997 | 6 | 8 |
| 4 | 2 | 2 | 1.963 | 1.963 | 4 | 4 |

Table 3. Uncertainties in these distances are about 0.01–0.03 Å.

Subsequent to the determination of this structure, we became aware of the powder pattern reported for a compound tentatively identified as CeZn_7 (Lott & Chiotti, 1966). We have been able to account for this pattern on the basis of $\text{Ce}_3\text{Zn}_{22}$, isostructural with $\text{Pu}_3\text{Zn}_{22}$. Cell constants are $a = 8.930 \pm 0.003$, $c = 21.36 \pm 0.01$ Å. Calculated intensities and d values for the first 40 lines are compared with the published values in Table 4. The remaining lines show an equally satisfactory agreement. Since the pattern was of a 76.53 wt. % zinc alloy and $\text{Ce}_3\text{Zn}_{22}$ corresponds to 77.4 wt % zinc, one would not be surprised to see extra lines arising from CeZn_5 . This may account for some of the discrepancies; for example, the 101 line of CeZn_5 has an intensity of 47 (out of 100) and would occur at $d = 3.155$, right on top of the 220 line of $\text{Ce}_3\text{Zn}_{22}$ which

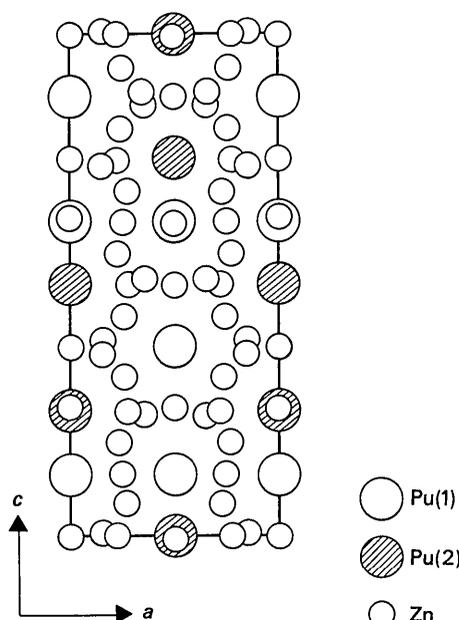


Fig. 1. Projection of $\text{Pu}_3\text{Zn}_{22}$ onto the ac plane. The centers of two of the hexagonal zinc sheaths (tubes) referred to in Fig. 2 are at $x = 1/2$, $z = 3/8$ and $x = 0$, $z = 7/8$. The axes of these tubes are normal to the plane of Fig. 1. Two more tubes related to the former by the 4_1 screw axis have axes lying in the plane of Fig. 1. These are not easily visualized. The centers of these tubes are at $z = 1/8$ and $5/8$.

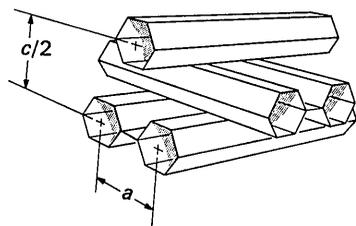


Fig. 2. Stacking of Pu(1)-containing zinc sheaths. Pu(2) atoms are located in the large cavities formed by this stacking.

was observed about 50% too strong. There is evidence, as well, for a phase at this approximate composition in the La–Zn, Pr–Zn, and Nd–Zn systems (Veleckis, Schablaske, Johnson & Feder, 1967). No diffraction patterns were reported, however.

Discussion

The structure of $\text{Pu}_3\text{Zn}_{22}$ bears a familial resemblance to the $D2_d$ and related structures such as ThMn_{12} (Florio, Rundle & Snow, 1952), $\text{Th}_2\text{Ni}_{17}$ (Florio, Baenziger & Rundle, 1956), $\text{Th}_2\text{Zn}_{17}$ (Makorov & Vinogradov, 1956), and $\text{Gd}_{13}\text{Zn}_{58}$ (Wang, 1967). Florio, Baenziger & Rundle (1956) noticed that ThMn_{12} and $\text{Th}_2\text{Ni}_{17}$ could be obtained from several $D2_d$ (CaZn_5 or AB_5) subcells; the larger cells and different stoichiometries were obtained by replacement of A atoms with pairs of B atoms. Thus, $6AB_5$ cells, in the case of the $\text{Th}_2\text{Ni}_{17}$ structure, becomes A_4B_{34} (A_2B_{17}) by the replacement of two A atoms with four B atoms. The general formula for these phases can be expressed as $A_{1-x}B_{5+2x}$. The values of x , which we will call the substitution parameter, and the structure type for $D2_d$ -related structures are given in Table 5.

Table 5. Substitution parameter for $D2_d$ -related structures

| x | Composition | Structure type |
|---------|----------------------|---|
| $-1/12$ | $A_{13/12}B_{4-5/6}$ | $\text{Gd}_{13}\text{Zn}_{58}$ |
| 0 | AB_5 | CaZn_5 |
| $1/4$ | $A_{3/4}B_{5-1/2}$ | $\text{Pu}_3\text{Zn}_{22}$ |
| $1/3$ | $A_{2/3}B_{5-2/3}$ | $\text{Th}_2\text{Zn}_{17}$; $\text{Th}_2\text{Ni}_{17}$ * |
| $1/2$ | $A_{1/2}B_6$ | ThMn_{12} |

* Johnson & Smith (1967) find that for the $\text{Th}_2\text{Ni}_{17}$ phase in the Ce–Mg system, $x = 0.43$.

In the case of $\text{Pu}_3\text{Zn}_{22}$ the integrity of the $D2_d$ subcell has been somewhat compromised, probably to effect more efficient packing. The replacement of A atoms by two B atoms is preserved, however, and is readily apparent in the structure.

The relation to, yet difference from, the $D2_d$ structure can be seen in Fig. 1, which is a projection of the structure onto the ac plane. In this Figure, one of the unusual aspects of the structure can be seen. Zinc atoms form hexagonal tubes surrounding Pu(1). The structure can be suitably described in terms of these tubes, the stacking of which is shown in Fig. 2. Pu(2) atoms are accommodated in the large cavities which are formed by this stacking.

This unusual arrangement achieves nearly identical environments for the two different plutonium atoms. The coordination polyhedra (C.P.) of these atoms are shown in Fig. 3. Pu(1) has 18 ligands, whereas Pu(2) has 20. In place of the two missing zinc atoms, Pu(1) has two Pu(1) neighbors (which are not considered as part of the C.P.) at a distance of 4.412 Å. The substitution of a pair of zinc atoms for a plutonium atom mentioned earlier accounts for this difference. Pu(1)

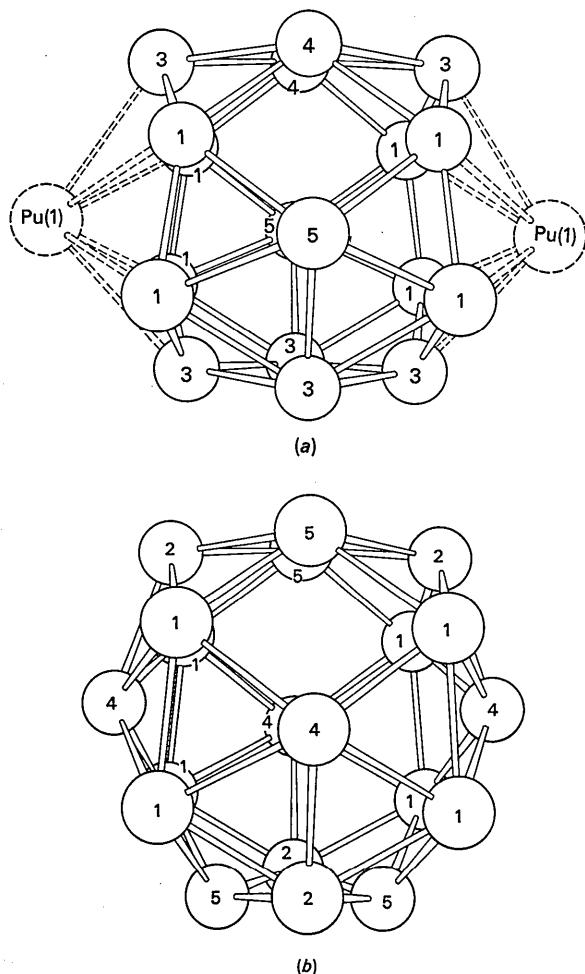


Fig. 3. (a) Coordination about Pu(1). Location of neighboring Pu(1) shown by dotted lines. These Pu(1)'s are too distant to be considered part of the coordination polyhedron, but are included to indicate the axis of the zinc sheaths pictured in Fig. 2. (b) Coordination about Pu(2). A pair of zinc atoms, Zn(4), takes the place of the Pu(1), shown by dotted lines in (a).

atoms could be pictured as constituting a one-dimensional chain contained within a zinc sheath. The C.P. of Pu(1) are fused together to form this continuous sheath because of the missing zinc pair.

There are no unusual C.P. encountered among the individual C.P. of zinc atoms. Zn(1) and Zn(2) have 12 ligands arranged in a distorted icosahedron. This distortion is caused, in the case of Zn(1), by three plutonium atoms and, in the case of Zn(2), by two plutonium atoms. There are 13 ligands surrounding Zn(3) in an arrangement similar to that of Ni(2) in the $\text{Th}_2\text{Ni}_{17}$ structure (Florio *et al.*, 1956). The C.P. for Zn(4) and Zn(5) could be thought of as half-way between the icosahedral arrangement of Zn(1) and Zn(2) and the thirteenfold ligancy of Zn(3). The extra atom in the Zn(4) C.P. is Zn(5) at a distance of 3.56 \AA , considerably longer than the average zinc-zinc distance. In analogous manner, Zn(5) has an extra Zn(4) in its C.P. at this same distance.

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References

- CRAMER, E. M. & WOOD, D. H. (1967). *J. Less-Common Metals*, **13**, 112.
 CROMER, D. T. (1965). *Acta Cryst.* **18**, 17.
 CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104.
 FLORIO, J. V., BAENZIGER, N. C. & RUNDLE, R. E. (1956). *Acta Cryst.* **9**, 367.
 FLORIO, J. V., RUNDLE, R. E. & SNOW, A. I. (1952). *Acta Cryst.* **5**, 449.
 JOHNSON, Q. & SMITH, G. S. (1967). *Acta Cryst.* **23**, 327.
 LOTT, B. G. & CHIOTTI, P. (1966). *Acta Cryst.* **20**, 733.
 MAKOROV, E. S. & VINOGRADOV, S. I. (1956). *Kristallografiya*, **1**, 634.
 SMITH, G. S., JOHNSON, Q. & NORDINE, P. C. (1965). *Acta Cryst.* **19**, 668.
 VELECKIS, E., SCHABLASKE, R. V., JOHNSON, I. & FEDER, H. M. (1967). *Trans. Met. Soc. AIME* **239**, 58.
 WANG, F. E. (1967). *Acta Cryst.* **22**, 579.