Acta Cryst. (1964). **17**, 947

The Crystal Structure of Pu_5Si_3*

BY DON T. CROMER, ALLEN C. LARSON AND R. B. ROOF, JR.

University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico, U.S.A.

Received 11 *September* 1963)

Pu_5Si_3 is isostructural with W_5Si_3. The unit cell is tetragonal, space group No. 140, $I4/mcm$, $a = 11{\cdot}409$, $c = 5{\cdot}448$ Å, and there are four formula units per unit cell. Least-squares refinement of counter data has been carried out.

Introduction

The plutonium-silicon binary system contains at least five compounds (Coffinberry & Miner, 1961). These are PuSi, Pu_2Si_3, $PuSi_2$ and two plutonium rich phases, one of which, Pu_5Si_3, is described in this paper. Pu_5Si_3 is isostructural with W_5Si_3, which has the $D8_m$ structure type.

Experimental

A plutonium alloy specimen containing 37 at.% silicon was prepared by co-melting the alloy constituents in an arc furnace and cooling the resulting ingot fairly rapidly to room temperature. Since Pu_5Si_3 contains 37·5 at.% silicon, the ingot contained a small amount of δ-Pu, which, under the microscope, was visible as a second phase between the Pu_5Si_3 grains. The ingot was crushed and small single-crystal fragments were selected for X-ray analysis. Preliminary precession photographs were taken which showed that the compound was probably isostructural with the W_5Si_3 or $D8_m$ structure type (Aronsson, 1955). Subsequent quantitative treatment verified this relationship with W_5Si_3. Crystallographic data are summarized in Table 1.

Table 1. *Crystallographic data for* Pu_5Si_3

Tetragonal, Space group No. 140, $I4/mcm$

$a = 11{\cdot}409 \pm 0{\cdot}003$ Å ($\lambda(\mathrm{Mo}K\alpha_1) = 0{\cdot}70926$ Å)
$c = 5{\cdot}448 \pm 0{\cdot}002$ Å

$Z = 4$
$D_x = 11{\cdot}98$ g.cm^{-3}
$D_m = 12{\cdot}0$ g.cm^{-3}

Unit-cell parameters and reflection intensities were measured with a carefully aligned single-crystal orienter on an XRD 5 apparatus, with Mo $K\alpha$ radiation. Background corrections were made by means of the balanced filter technique. The crystal selected for investigation had a maximum dimension of about 0·11 mm, which was in a direction approximately parallel to [110], the rotation axis. The entire hemisphere of the reciprocal lattice was investigated within a limiting sphere bounded by $2\theta_{\mathrm{Mo}} = 55°$. The shape of the crystal was approximated by six bounding plane faces. Absorption corrections were made by using the Busing & Levy (1957) method and Burnham's (1962) program which we modified for single-crystal orienter geometry. Transmisson factors varied from 0·26 to 0·44. After absorption corrections were applied the equivalent reflections (eight for the general *hkl* reflection) were averaged. An R index formed by comparing equivalent observed reflections was 5·3% based on F and 9·8% based on F^2. There were 223 non-equivalent observed reflections out of 244 possible.

Refinement of the structure

A least-squares refinement of the structure was made with the positions given by Aronsson (1955) for W_5Si_3

* Work performed under the auspices of the U.S. Atomic Energy Commission.

Table 2. *Coefficients for analytic form factor curves*

	a_1	b_1	a_2	b_2	a_3	b_3	a_4	b_4	c
Si	6·737	1·718	4·168	47·529	1·587	6·035	—	—	1·486
				$s = 0$ to 1·5 Å^{-1}					
Pu	36·576	0·497	23·790	3·223	16·679	14·156	3·405	93·209	5·23
				$s = 0$ to 1·99 Å^{-1} ($\Delta f' = -8{\cdot}26$)					

Table 3. *Final least-squares parameters for* Pu_5Si_3

Atom	Position set	x	y	z	$B_{11} \times 10^5$	$B_{22} \times 10^5$	$B_{33} \times 10^5$	$B_{12} \times 10^5$
Pu(1)	4(b)	0·0	0·5	0·25	248 ± 18	B_{11}	542 ± 96	
Pu(2)	16(k)	$0{\cdot}0855 \pm 0{\cdot}0001$	$0{\cdot}2208 \pm 0{\cdot}0001$	0·0	213 ± 15	199 ± 15	756 ± 49	10 ± 19
Si(1)	4(a)	0·0	0·0	0·25	103 ± 109	B_{11}	534 ± 675	
Si(2)	8(h)	$0{\cdot}1582 \pm 0{\cdot}0011$	$\frac{1}{2} + x$	0·0	197 ± 87	B_{11}	420 ± 190	11 ± 197

Extinction parameter: $g = 9{\cdot}55 \pm 0{\cdot}5 \times 10^{-8}$.

Table 4. *Observed and calculated structure factors for* Pu_5Si_3

The column headings are h, F_o and F_c. If F_o is negative the minus sign means 'less than'

K= 0 L= 0		K= 1 L= 3		K= 2 L= 4		K= 3 L= 6		K= 5 L= 2		K= 7 L= 1	
2	35 36	8	172 168	8	295 295	7	222 230	9	118 -112	8	136 126
4	325 383	10	354 350	10	-49 43			11	533 509	10	235 -222
6	318 -373	12	153 -155	12	152 -146	K= 4 L= 0		13	89 74	12	115 110
8	88 101										
10	408 447	K= 1 L= 4		K= 2 L= 5		4	95 -97	K= 5 L= 3		K= 7 L= 2	
12	281 288					6	37 -7				
14	407 396	1	63 -71	3	345 -360	8	101 79	6	171 168	7	615 605
		3	310 -320	5	146 149	10	279 298	8	-44 -3	9	121 -121
K= 0 L= 2		5	-40 21	7	55 -33	12	408 400	10	265 252	11	72 59
		7	472 -468	9	61 54	14	87 61	12	88 -85		
0	914 888	9	145 144							K= 7 L= 3	
2	610 -595	11	253 -244	K= 2 L= 6		K= 4 L= 1		K= 5 L= 4			
4	246 -231									8	118 110
6	900 -829	K= 1 L= 5		2	372 -399	5	325 326	5	600 -596	10	204 -196
8	325 -328			4	74 77	7	225 -224	7	80 -69		
10	88 64	2	189 -190	6	-48 15	9	226 -233	9	299 -302	K= 7 L= 4	
12	-46 -17	4	378 -393			11	-42 8	11	245 246		
14	146 142	6	146 145	K= 3 L= 0		13	-51 -38			7	273 275
		8	128 128					K= 5 L= 5		9	298 -290
K= 0 L= 4		10	271 272	3	268 -291	K= 4 L= 2					
				5	-33 23			6	123 127	K= 8 L= 0	
0	1090 1108	K= 1 L= 6		7	63 63	4	598 -594	8	-47 -2		
2	48 28			9	209 -225	6	457 -456			8	146 144
4	245 257	1	193 206	11	231 -254	8	323 -314	K= 5 L= 6		10	111 131
6	254 -250	3	48 24	13	171 -172	10	68 -48			12	188 189
8	84 79	5	232 244			12	109 107	5	219 -224		
10	359 343	7	126 -132	K= 3 L= 1						K= 8 L= 1	
12	236 227					K= 4 L= 3		K= 6 L= 0			
		K= 2 L= 0		4	-32 14					9	273 -268
K= 0 L= 6				6	368 366	5	273 269	6	601 620	11	157 -148
		2	162 -180	8	644 -671	7	192 -189	8	178 210		
0	398 429	4	604 809	10	91 94	9	208 -202	10	49 -30	K= 8 L= 2	
2	293 -309	6	469 582	12	180 -183	11	-43 7	12	183 190		
4	119 -131	8	346 395	14	276 296					8	183 -174
6	443 -465	10	63 52			K= 4 L= 4		K= 6 L= 1		10	152 -140
		12	194 -192	K= 3 L= 2							
K= 1 L= 0		14	161 142			4	71 -59	7	212 205	K= 8 L= 3	
				3	176 170	6	-42 0	9	288 280		
1	89 -102	K= 2 L= 1		5	407 400	8	71 63	11	70 67	9	240 -235
3	393 -486			7	398 384	10	238 232	13	114 -109		
5	-34 40	3	674 -638	9	78 64					K= 8 L= 4	
7	539 -648	5	245 247	11	-43 -13	K= 4 L= 5		K= 6 L= 2			
9	176 199	7	52 -51	13	-50 19					8	124 114
11	307 -312	9	80 82			5	196 200	6	172 167		
13	93 70	11	184 189	K= 3 L= 3		7	145 -144	8	165 -156	K= 9 L= 0	
		13	226 -224			9	150 -156	10	343 -325		
K= 1 L= 1				4	-37 11			12	76 -67	9	68 -64
		K= 2 L= 2		6	306 304	K= 4 L= 6				11	82 93
2	369 -347			8	589 -572			K= 6 L= 3			
4	726 -683	2	807 -764	10	85 82	4	320 -333			K= 9 L= 1	
6	232 238	4	170 162	12	162 -161	6	253 -268	7	173 176		
8	189 198	6	57 41					9	248 244	10	275 -251
10	373 404	8	70 -50	K= 3 L= 4		K= 5 L= 0		11	68 59		
12	170 -176	10	298 -296							K= 9 L= 2	
14	123 -120	12	453 -462	3	202 -199	5	790 -828	K= 6 L= 4			
		14	103 -93	5	-40 11	7	72 -87			9	152 133
K= 1 L= 2				7	54 41	9	341 -391	6	473 462		
		K= 2 L= 3		9	185 -174	11	300 321	8	164 163	K= 10 L= 0	
1	377 395			11	207 -200	13	109 -101	10	-47 -20		
3	41 26	3	508 -503							10	237 210
5	453 436	5	204 202	K= 3 L= 5		K= 5 L= 1		K= 6 L= 5			
7	252 -247	7	58 -43							K= 10 L= 2	
9	466 469	9	76 70	4	-42 8	6	197 198	7	135 135		
11	68 -58	11	166 166	6	227 227	8	-41 -3			10	-51 -29
13	267 253	13	208 -199	8	432 -437	10	288 288	K= 7 L= 0			
				10	78 64	12	102 -96				
K= 1 L= 3		K= 2 L= 4						7	368 370		
				K= 3 L= 6		K= 5 L= 2		9	327 -369		
2	267 -271	2	108 -110					11	136 -136		
4	549 -544	4	545 544	3	101 97	5	410 -409	13	366 -369		
6	204 195	6	416 413	5	218 229	7	224 217				

as starting parameters. The function minimized was $\Sigma w(\Delta F)^2$ with w determined from the counting statistics according to the method derived by Evans (1961). Unobserved reflections were given zero weight. The silicon form factor was that given in *International Tables for X-ray Crystallography* (1962). A recently calculated relativistic plutonium form factor was used and to this a $\Delta f'$ correction of $-8{\cdot}26$ electrons was applied.* The scattering curves were used in the functional form

$$f(s) = \sum_{i=1}^{n} a_i \exp(-b_i s) + c$$

where $s = \sin\theta/\lambda$, and $n=3$ for silicon and $n=4$ for plutonium. The coefficients are given in Table 2. A secondary extinction parameter was also included so that the observation equations were of the form

$$\Delta F = |F_{obs}| - \frac{K|F_c|}{\sqrt{\left(1 + g\,\mathrm{Lp}\left(\frac{2(1+\cos^4 2\theta)}{(1+\cos^2 2\theta)^2}\right)|F_c|^2\right)}}$$

where g is the extinction parameter (Zachariasen, 1963).

Isotropic least-squares calculations were made first. These calculations showed that Pu_5Si_3 was indeed isostructural with W_5Si_3. Finally, anisotropic calculations were made, and the final parameters are given in Table 3. After the last cycle the changes as fractions of the standard deviations were $< 6\times10^{-4}$ for position parameters, $< 2\times10^{-3}$ for thermal parameters and $1{\cdot}5\times10^{-2}$ for the extinction parameter. Observed and calculated structure factors are given in Table 4. The final R index with unobserved reflections omitted is 5·4%.

Discussion

The interatomic distances in Pu_5Si_3 are listed in Table 5. The standard deviations given in the table were computed with correlation terms included but no account was taken of possible errors in the lattice constant values.

The anisotropic thermal parameters were transformed to obtain the axes and orientations of the thermal ellipsoids. These quantities are given in Table 6. Pu(2) and Si(1) have essentially isotropic thermal motion. Pu(1) and Si(2) have a significantly larger amplitude in the xy plane than they have parallel to z. The reason for the anistropy of Pu(1) is clear, for these atoms lie rather close together in a linear chain parallel to z and, hence, can vibrate most easily in a direction normal to this chain. There is no obvious constraint on the motion of Si(2).

Table 5. *Interatomic distances in* Pu_5Si_3

Pu(1)–4 Si (2)	2·893 ± 0·015 Å	Si(1)–2 Si (1)	2·724 ± 0·0 Å
–2 Pu(1)	2·724 ± 0·0	–8 Pu(2)	3·025 ± 0·001
–8 Pu(2)	3·599 ± 0·002		
Pu(2)–2 Si (1)	3·025 ± 0·001	Si(2)–2 Si (2)	4·025 ± 0·025
–1 Si (2)	3·010 ± 0·015	–2 Pu(1)	2·893 ± 0·015
–1 Si (2)	3·104 ± 0·006	–2 Pu(2)	3·010 ± 0·015
–2 Si (2)	3·164 ± 0·002	–2 Pu(2)	3·104 ± 0·006
–2 Pu(1)	3·599 ± 0·002	–4 Pu(2)	3·164 ± 0·002
–1 Pu(2)	3·125 ± 0·003		
–2 Pu(2)	3·351 ± 0·002		
–2 Pu(2)	3·491 ± 0·002		
–2 Pu(2)	3·820 ± 0·002		

Table 6. *Thermal ellipsoids in* Pu_5Si_3

Atom	Axis	r.m.s. Amplitude	Orientation relative to the crystallographic axes: *a*	*b*	*c*
Pu(1)	1	0·128 ± 0·005 Å	0°	90°	90°
	2	0·128 ± 0·005	90	0	90
	3	0·090 ± 0·008	90	90	0
Pu(2)	1	0·119 ± 0·004	17 ± 32	73 ± 32	90
	2	0·114 ± 0·004	107 ± 32	17 ± 32	90
	3	0·107 ± 0·003	90	90	0
Si(1)	1	0·116 ± 0·038	45	45	90
	2	0·112 ± 0·038	135	45	90
	3	0·079 ± 0·046	90	90	0
Si(2)	1	0·083 ± 0·043	0	90	90
	2	0·083 ± 0·043	90	0	90
	3	0·090 ± 0·057	90	90	0

A difference Fourier synthesis was computed in order to determine if any significant features remained. The sections at $z=0$ and $\frac{1}{4}$ are shown in Figs. 1 and 2. The only feature of significance is the hole of $\sim$12 e.Å^{-3} at 0, $\frac{1}{2}$, 0, the point half-way between the Pu(1) atoms. The negative region extends all along the line 0, $\frac{1}{2}$, z

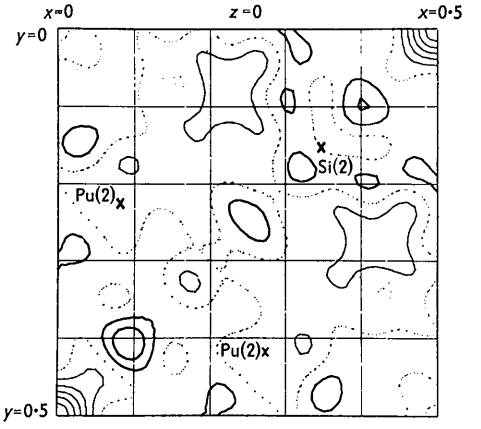

Fig. 1. Difference Fourier section at $z=0$. Contours are at 2·0 e.Å^{-3}, the approximate standard deviation of the electron density. Positive contours are heavy lines and negative contours light lines. The zero contour is dotted.

and the hole may be accounted for by the closeness of the Pu atoms. In computing the difference Fourier synthesis, two overlapping spheres are subtracted and

* Tables of scattering factors and anomalous dispersion terms calculated from relativistic wave functions are in preparation.

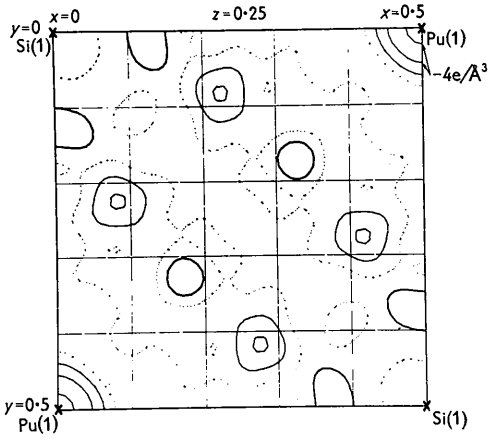

Fig. 2. Difference Fourier section at $z=0{\cdot}25$ for Pu_5Si_3. Contours as in Fig. 1.

thus, in the overlapping region, too much electron density was removed.

All calculations were performed with an IBM 7090 or 7094 with programs written by the authors. We wish to thank Mr. V. O. Struebing for preparing the specimen.

References

ARONSSON, B. (1955). *Acta Chem. Scand.* **9**, 137.
BURNHAM, C. W. (1962). I.U.Cr. *World List of Crystallographic Computer Programs*, Program 338.
BUSING, W. R. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 180.
COFFINBERRY, A. S. & MINER, W. N. (1961). *The Metal Plutonium*. Chap. XXV by Ellinger, F. H. Univ. of Chicago Press.
EVANS, H. T. (1961). *Acta Cryst.* **14**, 689.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
ZACHARIASEN (1963). *Acta Cryst.* **16**, 1139.

Acta Cryst. (1964). **17**, 950

Anomalous Transmission of X-rays in an Elastically Deformed Non-Isotropic Crystal

BY D. POLDER AND P. PENNING

Philips Research Laboratories, N. V. Philips' Gloeilampenfabrieken, Eindhoven, The Netherlands

(*Received* 12 *August* 1963)

A point source of X-rays placed before a slice of dislocation-free germanium produces on a photographic plate behind the slice a picture that is characteristic of the anomalous transmission of the X-rays. The change in this picture due to bending of the germanium slice is explained theoretically in this paper. The characteristic features of the change are related with the fact that germanium is an elastically non-isotropic material.

Introduction

The aim of this paper is to account for certain phenomena connected with anomalous transmission of X-rays through elastically deformed perfect crystals that have been observed by van Bommel (1964) in this laboratory. In his experiments a thin slice of a dislocation-free germanium crystal was irradiated with X-rays from a point source located near the surface of the crystal. A photographic plate some distance away from the opposite surface then clearly indicates the directions in which anomalous propagation of X-ray energy is possible through the crystal. In particular, if the [111] axis of the crystal is perpendicular to the surface, a picture with sixfold symmetry is obtained, which reveals anomalous transmission of X-rays along (220) planes of the germanium lattice. Van Bommel observed that bending of the crystal results in a characteristic change of the picture on the photographic plate as a result of increased absorption of the X-rays. For instance, bending can destroy the sixfold symmetry of the picture and can produce apparent threefold symmetry. It will be shown in this paper that these experimental results can be understood from the general theory developed in a previous paper (Penning & Polder, 1961) and that they are intimately connected with the cubic anisotropy of the tensor of the elastic compliance of germanium.

Resumé of the general theory

In our previous paper it was emphasized that anomalous transmission of X-rays is connected with the fact that electromagnetic energy cannot propagate as a plane wave in an infinite medium with a dielectric