reported also in other substances in which the bisector of the lone-pairs is directed toward a metal ion or toward a hydrogen bond donor group (Chidambaram, Sequeira & Sikka, 1964).

The replacement of hydrogen by deuterium should have very little effect on the lattice energy if the crystal structure is the same. The major effect of the replacement then will be the difference in the zero point energy. In a flat and highly asymmetric potential field in which the hydrogen atom moves, the higher zero point energy of the proton will be associated with an increase of the OH length over the OD. The difference in the zero point energy affects the strength of the hydrogen bond, as indicated theoretically by Gallagher (1959) and Reid (1959). In the case of oxalic acid dihydrate, however, the difference of the vibration energy is so large that the effect is not sufficiently compensated by the elongation of the short hydrogen bond alone but necessitates a transformation into a more stable crystal structure. In α-$(COOH)_2.2H_2O$, the hydrogen bond between the hydroxyl group of the oxalic acid molecule and the oxygen atom of the water molecule is strong enough for one of the lone-pairs to be specifically directed toward the donor group. In β-$(COOD)_2.2D_2O$, on the other hand, the corresponding hydrogen bond is slightly weaker so that it seems to be rather unfavorable for only one of the lone-pairs to be specifically directed. Consequently the bisector of two lone-pairs is directed toward a hydrogen donor group These small changes in the interatomic force seems to alter the entire crystal structure.

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The Crystal Structure of $Pu_2Zn_{\sim 9}$*

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$Pu_2Zn_{\sim 9}$ has a hexagonal subcell with $a=14{\cdot}43$ and $c=14{\cdot}14$ Å, probable space group $P6_3/mmc$. The true unit cell appears to be hexagonal with a doubled a axis but this apparent hexagonal symmetry may result from twinning. A reasonable solution has been obtained for the subcell and leads to the formula $Pu_{13}Zn_{58}$ or $PuZn_{4{\cdot}46}$. The subcell is similar to and probably isostructural with recently reported phases $Ce_2Cd_{\sim 9}$, $Ce_2Zn_{\sim 9}$ and $Y_2Zn_{\sim 9}$.

Introduction

As part of an investigation of binary phase diagrams being carried out in this Laboratory, the Pu–Zn system has been studied. Four zinc-rich phases, $PuZn_2$, $Pu_2Zn_{\sim 9}$, $PuZn_8$ and Pu_2Zn_{17} have been reported by Cramer, Ellinger & Land (1960). Recently, Cramer & Wood (1966) have found evidence of other phases in the high-zinc region of the phase diagram. The rather complex phase $Pu_2Zn_{\sim 9}$ is the subject of the present report.

While this work was in progress, Elliott & Lemons (1964) found, through vapor pressure measurements, a series of 'microphases' in the Ce–Cd system near

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Ce_2Cd_9. Roof & Elliott (1965) in an X-ray study of these microphases found a hexagonal subcell with a number of different superlattices. $Pu_2Zn_{\sim 9}$ has a subcell apparently isomorphous with $Ce_2Cd_{\sim 9}$. However, only one type of superlattice has been observed in $Pu_2Zn_{\sim 9}$, and this superlattice is different from any observed in $Ce_2Cd_{\sim 9}$. Renewed impetus for study of the $Pu_2Zn_{\sim 9}$ structure was given by the discovery of the similarity between these two systems.

Lott & Chiotti (1966) have recently studied the Ce–Zn system and have found a compound $Ce_2Zn_{\sim 9}$ which has a unit cell similar to the $Pu_2Zn_{\sim 9}$ subcell. Also, they reported that an analogous yttrium compound probably exists. We have computed powder patterns for $Ce_2Zn_{\sim 9}$ and $Y_2Zn_{\sim 9}$ using our final parameters for $Pu_2Zn_{\sim 9}$ and these computed patterns are reported by Harsha (1966) to be in good agreement with the observed patterns. No superlattice has so far been observed in $Ce_2Zn_{\sim 9}$ and $Y_2Zn_{\sim 9}$.

Experimental

An alloy of nominal composition $PuZn_{4\cdot5}$ was prepared by the method of Cramer *et al.* (1960). Metallographic examination showed the button to be predominantly a single phase. Recent metallographic studies of this phase by Cramer & Wood (1966) have shown pronounced twinning.

Specimens, presumed to be single crystals, were examined by Laue and precession photography. The observed Laue symmetry is $6/mmm$. Lattice constants were measured on a General Electric Co. single-crystal orienter with an XRD-5 spectrogoniometer using Mo radiation ($\lambda\, K\alpha_1 = 0{\cdot}70926$ Å) and are $a = 28{\cdot}86 \pm 0{\cdot}02$ and $c = 14{\cdot}14 \pm 0{\cdot}01$ Å, with a pronounced subcell having $a = 14{\cdot}43$ Å and the same c axis. The symmetry of the subcell is apparently that of space group $P6_3/mmc$, if centric, or $P6_3mc$ or $P\bar{6}2c$ if non-centric, for reflections hhl with $l = 2n+1$ are absent or weak. The few weak reflections that violate the above extinction rule are similar in intensity to those few weak reflections that double the a axis of the subcell. The assumption has been made in the present analysis that the weak hhl reflections in the subcell which violate the extinction rule originate from the large unit cell with doubled a axis. Although no evidence for Laue symmetry lower than $6/mmm$ has been found for the true unit cell, in view of the twinning observed by Cramer & Wood (1966) and the clear evidence of orthorhombic and monoclinic superlattices found by Roof & Elliott (1965) in $Ce_2Cd_{\sim 9}$, it is very possible that the true unit cell has lower symmetry.

Many crystals were examined from three different preparations. No evidence for microphases such as were observed in the Ce–Cd system was found. All crystals had the same, doubled hexagonal unit cell, and all showed the same violations of the c glide. Vapor pressure measurements of the type which first detected the Ce–Cd microphases have not been made.

The density of the bulk sample was found to be 9·05 g.cm^{-3}. Calculated densities for subcells containing $Pu_{26}Zn_{116}$, $Pu_{26}Zn_{118}$, $Pu_{26}Zn_{120}$ are 8·98, 9·06 and 9·15 g.cm^{-3} respectively.

Intensity measurements were made by the stationary-crystal, stationary-counter, fixed-time method with the single-crystal orienter using Zr-filtered Mo $K\alpha$ radiation. Three sets of data in the range $2\theta \leq 50°$ were collected at various times and were in substantial agreement. The first and third sets contained all reflections; the second set contained only reflections of the subcell. The subcell reflections of data set three were subsequently used in the detailed analysis. The crystal used was approximated to be a sphere of 0·035 *mm* radius ($\mu R = 1{\cdot}7$), and an absorption correction was approximated by the φ and sphere method (Larson & Cromer, 1962; Larson, Cromer & Roof, 1964, LA-3043). Long after these data had been collected it was noticed that three reasonably strong reflections (052, 083 and 0,11,4)

Table 1. *Least-squares parameters for* $Pu_2Zn_{\sim 9}$

Standard deviations, in parentheses, apply to the rightmost digit

	x	y	z	$\beta_{11}\times10^4$	$\beta_{22}\times10^4$	$\beta_{33}\times10^4$	$\beta_{12}\times10^4$	$\beta_{13}\times10^4$	$\beta_{23}\times10^4$
Pu(1)	0	0	0	38 (6)	β_{11}	53 (8)	β_{11}	—	—
Pu(2)	0·2062 (2)	$-x$	0·0518 (3)	29 (2)	β_{11}	18 (2)	32 (6)	−6 (2)	$-\beta_{13}$
Pu(3)	0·5415 (3)	$-x$	$\frac{1}{4}$	29 (3)	β_{11}	22 (3)	31 (8)	—	—
Pu(4)	0·8730 (4)	$-x$	$\frac{1}{4}$	27 (4)	β_{11}	172 (11)	36 (10)	—	—
Zn(1)	0	0	$\frac{1}{4}$	32 (17)	β_{11}	29 (21)	β_{11}	—	—
Zn(2)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{3}{4}$	0 (13)	β_{11}	50 (25)	β_{11}	—	—
Zn(3)	$\frac{1}{3}$	$\frac{2}{3}$	0·0956 (15)	12 (8)	β_{11}	0 (9)	β_{11}	—	—
Zn(4)	0·3663 (10)	0·0334 (8)	0·1005 (7)	60 (10)	23 (8)	21 (4)	17 (12)	−12 (12)	42 (11)
Zn(5)	0·0963 (7)	$-x$	0·1573 (12)	45 (10)	β_{11}	44 (10)	74 (23)	12 (9)	$-\beta_{13}$
Zn(6)	0·0856 (11)	0·3674 (11)	$\frac{1}{4}$	14 (9)	β_{11}	19 (7)	2 (16)	—	—
Zn(7)	0·4371 (6)	$-x$	0·1416 (10)	29 (8)	β_{11}	13 (6)	42 (18)	−15 (6)	$-\beta_{13}$
Zn(8)	0·6008 (6)	$-x$	0·0548 (10)	19 (7)	β_{11}	18 (6)	26 (16)	0 (7)	$-\beta_{13}$
Zn(9)	0·7630 (6)	$-x$	0·1573 (9)	22 (7)	β_{11}	9 (6)	13 (18)	5 (7)	$-\beta_{13}$
Zn(10)	0·2706 (9)	$-x$	$\frac{1}{4}$	33 (12)	β_{11}	7 (9)	36 (28)	—	—
Zn(11)	0·1986 (16)	0	0	68 (13)	127 (27)	170 (25)	β_{22}	114 (23)	$2\beta_{13}$
Zn(12)	$\frac{1}{2}$	0	0	97 (24)	9 (16)	72 (18)	β_{22}	8 (16)	$2\beta_{13}$

$g = 1{\cdot}2 \pm 12 \times 10^{-9}$

were missing from this third data set, apparently because of a setting error when they were measured. These reflections were present in the other data sets and on all appropriate films.

Determination and refinement of the subcell structure

The space group of the subcell was assumed to be $P6_3/mmc$ and the ultimate structure factor agreement shows that this assumption is at least a very good approximation. For least-squares refinement the quantity minimized was $\Sigma w(F_o - F_c^*)^2$ with $w=0$ for unobserved reflections and for those few *hhl* reflections with $l=2n+1$ which violate the assumed space group. For all other reflections $w=1$. Reflections were considered to be observed if $(I-\text{Background}) \geq 2{\cdot}5(I+\text{Background})^{\frac{1}{2}}$; otherwise the intensity was assumed to be less than $2{\cdot}5(I+\text{Background})^{\frac{1}{2}}$. R indices quoted are $\Sigma \, ||F_o|-|F_c^*|| / \Sigma \, |F_o|$ with unobserved reflections and observed *hhl* reflections with $l=2n+1$ omitted. In the above,

$$F_c^* = KF_c / \left\{ 1 + g \left[\frac{2(1+\cos^4 2\theta)}{(1+\cos^2 2\theta)^2} \right] \mathrm{Lp}\, F_c^2 \right\}^{\frac{1}{4}},$$

Table 2. *Observed and calculated structure factors for* $Pu_2Zn_{\sim 9}$

Column headings are l, F_o/K and F_c^*/K (see text).
A minus sign preceding F_o means 'less than'.

H= 0 K= 0		H= 0 K= 5		H= 0 K= 11		H= 1 K= 3		H= 1 K= 8		H= 2 K= 3	
1	-74	0	4	-102	71	0	-136	153	4	226	214	13	-127	-86	0	-87	-99
2	-70	29	5	202	184	1	139	-83	5	94	47	14	-125	-18	1	108	-55
3	-79	0	6	178	149	2	430	-436	6	-82	-2				2	440	-407
4	893	937	7	-110	17	3	263	246	7	105	17	H= 1 K= 9			3	1327	1308
5	-90	0	8	854	-899	4	-139	406	8	271	288				4	-96	93
6	1089	-1041	9	156	185	5	-135	58	9	-96	7	0	-104	-53	5	203	179
7	-115	0	10	298	-298	6	-143	-106	10	123	-45	1	-113	-6	6	-106	111
8	658	634	11	138	-77	7	255	297	11	-115	37	2	-106	83	7	606	589
9	-113	0	12	514	-492	8	496	528	12	-111	8	3	-115	-28	8	192	216
10	1369	-1378	13	208	-170	9	-143	71	13	-116	-34	4	-109	117	9	307	-274
11	-145	0	14	-142	158	10	-128	-86	14	-127	99	5	-111	13	10	384	358
12	492	489	15	-146	11	11	-161	-99	15	-122	-138	6	-113	143	11	179	172
13	-128	0	16	-158	91	12	405	418	16	153	153	7	-123	71	12	162	184
14	384	-458										8	-116	73	13	485	-488
15	-133	0	H= 0 K= 6			H= 0 K= 12		H= 1 K= 4				9	-118	-29	14	-140	64
16	274	254										10	-130	61	15	-138	-125
17	-129	0	0	306	-263	0	176	-206	0	-84	-69	11	-124	-25	16	152	-132
			1	162	-112	1	278	234	1	507	535	12	-127	38			
H= 0 K= 1			2	576	572	2	-136	65	2	153	108	13	-127	44	H= 2 K= 4		
			3	107	-138	3	-137	42	3	129	-63						
0	-76	-44	4	-104	-71	4	-130	-45	4	286	307	H= 1 K= 10			0	378	352
1	-69	-26	5	776	770	5	-132	48	5	-89	48				1	90	63
2	-94	32	6	144	111	6	280	229	6	147	161	0	165	145	2	-86	56
3	294	303	7	122	-115	7	110	57	7	115	-193	1	115	-193	3	-102	-422
4	190	238	8	155	200	8	-127	57	8	163	160	2	-112	-41	4	401	408
5	217	191	9	-119	-96	9	-154	136	9	257	244	3	137	42	5	-95	7
6	355	416	10	871	855	10	-166	205	10	202	159	4	337	-345	6	-94	91
7	-98	72	11	-125	122				11	295	-223	5	170	-160	7	-104	-100
8	158	106	12	-129	127	H= 0 K= 13			12	-129	53	6	398	377	8	141	160
9	144	56	13	149	-100				13	140	-9	7	-118	-25	9	-113	117
10	290	290	14	-144	3	0	211	-186	14	-129	37	8	205	190	10	-111	67
11	130	24	15	248	-289	1	133	-22	15	-124	-9	9	-110	-100	11	-128	-116
12	-129	36				2	212	-242	16	-126	5	10	184	141	12	-121	94
13	-145	-151	H= 0 K= 7			3	582	-574				11	-127	53	13	199	172
14	179	101				4	214	204	H= 1 K= 5			12	217	190	14	-129	-6
15	-125	-114	0	312	-288	5	-136	-202							15	-134	-12
16	-152	-58	1	207	-223	6	-145	79	0	333	339	H= 1 K= 11			16	-131	97
17	-150	3	2	363	-348	7	191	-265	1	242	220						
			3	-101	296	8	-156	234	2	361	-347	0	140	148	H= 2 K= 5		
H= 0 K= 2			4	247	243	9	-132	-63	3	-82	-43	1	140	-93			
			5	146	134				4	339	329	2	198	232	0	168	-193
0	-88	-26	6	-134	146	H= 0 K= 14			5	-89	48	3	223	261	1	629	-667
1	-93	-20	7	554	574				6	156	-94	4	117	-63	2	171	150
2	174	-174	8	372	343	0	-145	56	7	326	-344	5	-118	70	3	101	-70
3	474	511	9	-121	-71	1	-145	-4	8	632	601	6	-120	49	4	208	-192
4	162	193	10	-132	86	2	289	249	9	-105	-101	7	-122	6	5	603	-591
5	596	595	11	144	-183	3	-138	56	10	-110	-60	8	-133	-120	6	386	388
6	140	153	12	-151	15	4	-154	176	11	-113	98	9	-126	-173	7	116	-96
7	616	584	13	400	-419	5	-148	-1	12	342	321	10	-128	-5	8	226	209
8	625	648	14	190	185	6	-138	94	13	175	198	11	-125	88	9	321	-277
9	168	170	15	-145	-21	7	-138	55	14	-127	-126				10	131	114
10	234	230							15	187	150	H= 1 K= 12			11	381	374
11	360	-328	H= 0 K= 8			H= 0 K= 15			16	-137	170				12	196	201
12	323	293										0	-120	80	13	176	160
13	334	-364	0	-116	39	0	466	499	H= 1 K= 6			1	145	35	14	148	118
14	-121	27	1	-111	-7	1	-145	118				2	205	206	15	265	269
15	385	-358	2	-135	125	2	-135	125	0	102	79	3	206	-193			
16	-146	92	3	-107	-1068	3	-133	-73	1	103	51	4	-122	-104	H= 2 K= 6		
17	-134	-62	4	212	219				2	104	146	5	-123	-25			
			5	235	-234	H= 1 K= 1			3	150	127	6	-134	60	0	296	321
H= 0 K= 3			6	182	155				4	154	124	7	-114	115	1	169	165
			7	651	-611	0	-74	-20	5	-93	27	8	-115	-90	2	698	748
0	444	-407	8	216	253	1	-67	0	6	165	160	9	-129	7	3	188	164
1	526	-517	9	172	162	2	-84	71	7	-114	-66	10	-129	-55	4	-92	7
2	196	210	10	287	286	3	-80	0	8	-105	-82				5	198	189
3	198	237	11	-138	-109	4	105	86	9	-113	98	H= 1 K= 13			6	198	107
4	408	-362	12	282	265	5	130	0	10	-113	-110				7	212	-220
5	1987	-2035	13	462	418	6	329	303	11	-115	28	0	-133	-119	8	349	-344
6	466	-426	14	-156	128	7	-95	0	12	-106	-3	1	281	328	9	-109	6
7	219	169				8	-96	-29	13	-121	-106	2	-124	81	10	-112	-92
8	340	338	H= 0 K= 9			9	-102	0	14	-113	20	3	-125	6	11	-115	-57
9	210	-194				10	181	-114	15	-128	-47	4	-126	-53	12	225	-227
10	920	947	0	796	829	11	-113	0				5	153	93	13	232	265
11	189	213	1	197	-231	12	-112	74	H= 1 K= 7			6	-128	-85	14	-125	51
12	220	232	2	-118	-9	13	-123	0				7	-129	58	15	148	-135
13	-135	80	3	-130	139	14	137	137	0	481	518	8	-110	69			
14	256	-208	4	-122	51	15	-140	0	1	282	-271				H= 2 K= 7		
15	627	709	5	162	-136	16	-138	4	2	-93	-91						
16	157	-169	6	-120	68	17	-118	0	3	139	-126	H= 1 K= 14			0	159	157
17	-130	-20	7	138	131				4	533	545				1	113	-51
			8	-149	178	H= 1 K= 2			5	146	127	0	-128	65	2	114	57
H= 0 K= 4			9	-135	-98				6	572	-564	1	-138	16	3	-96	-64
			10	180	-178	0	198	245	7	202	-191	2	-129	33	4	-98	19
0	-112	204	11	134	111	1	-77	57	8	133	132	3	-130	83	5	178	166
1	93	150	12	-151	101	2	453	499	9	167	-164	4	-128	-24	6	-104	2
2	265	300	13	-140	-112	3	-89	13	10	171	-231	5	149	-105	7	-107	102
3	549	-511	14	-131	5	4	91	15	11	142	137				8	-110	114
4	471	491				5	108	38	12	-121	-23	H= 2 K= 2			9	-128	36
5	141	139	H= 0 K= 10			6	96	16	13	-133	50				10	139	-118
6	444	459				7	173	-172	14	-137	-176	0	487	505	11	-117	25
7	-111	-35	0	519	462	8	389	-344	15	-109	-42	1	-76	0	12	-109	-67
8	205	202	1	280	-263	9	-105	-50				2	-82	64	13	150	-100
9	175	85	2	862	858	10	250	-268	H= 1 K= 8			3	85	0	14	-127	46
10	130	-73	3	-120	30	11	152	-100				4	755	799			
11	235	-253	4	167	313	12	-127	-155	0	-105	26	5	90	0	H= 2 K= 8		
12	-144	185	5	-136	-83	13	270	275	1	-105	42	6	302	-257			
13	-148	192	6	199	196	14	-132	-6	2	146	-139	7	101	0	0	148	-194
14	-147	10	7	-127	130	15	-137	-76	3	462	470	8	-105	55	1	792	816
15	-144	-22	8	492	-516	16	-134	70	4	-102	139	9	112	0	2	123	85
16	-141	53	9	-132	108	17	-127	-7	5	-105	-63	10	-123	30	3	-103	53
			10	320	-324				6	131	-61	11	-114	-6	4	-113	9
H= 0 K= 5			11	-145	-29	H= 1 K= 3			7	-111	78	12	-121	66	5	649	621
			12	272	-265				8	137	-133	13	-132	0	6	163	176
0	849	850	13	149	-163	0	-89	-21	9	198	-171	14	-130	-31	7	135	98
1	199	210				1	96	-30	10	142	160	15	-141	0	8	137	200
2	-90	1733				2	140	-136	11	-121	141	16	210	215	9	382	384
3	485	-457				3	202	166	12	-124	97				10	285	280

H= 2 K= 8		H= 3 K= 4		H= 3 K= 10		H= 4 K= 7		H= 5 K= 7		H= 6 K= 8	
11	450	-452	5	146	138	5	141	170	10	142	133	0	-117	-198	2	-121	-60
12	150	117	6	148	209	6	-118	87	11	253	-334	1	125	-95	3	168	164
13	-127	-94	7	160	132	7	564	528	12	-124	6	2	178	-164	4	-137	157
			8	342	-316	8	277	240	13	-112	51	3	-125	86	5	-132	100
H= 2 K= 9			9	149	151	9	-125	-22				4	-114	73	6	-134	39
			10	155	-110	10	-127	24	H= 4 K= 8			5	185	169	7	177	235
0	159	172	11	131	-45	11	-119	-49				6	-125	6	8	-150	171
1	184	195	12	193	-151				0	298	286	7	235	231	9	237	51
2	-109	65	13	141	-159	H= 3 K= 11			1	-105	60	8	219	207	10	-138	-4
3	-110	-131	14	-137	80				2	128	164	9	-126	18			
4	-112	6	15	-133	-50	0	-118	41	3	-115	84	10	205	156	H= 6 K= 9		
5	-121	-116				1	-118	87	4	-123	-8	11	149	-144			
6	-114	46	H= 3 K= 5			2	-127	-155	5	210	-178	12	-141	95	0	-133	46
7	295	-344				3	352	-383	6	-120	58				1	-133	69
8	140	116	0	160	-157	4	145	144	7	218	-231	H= 5 K= 8			2	-136	-64
9	-119	-29	1	144	-114	5	-121	0	8	-125	66				3	-127	-11
10	-121	-6	2	342	-305	6	123	47	9	144	-122	0	308	-277	4	204	163
11	150	79	3	536	578	7	301	-289	10	-139	-102	1	610	-622	5	-121	-73
12	154	84	4	-96	-21	8	-127	27	11	-125	17	2	-124	-2	6	-146	30
13	225	213	5	483	475	9	-133	134	12	-124	-10	3	-131	2	7	-141	-24
			6	-102	9							4	316	-258	8	-142	123
H= 2 K= 10			7	744	720	H= 3 K= 12			H= 4 K= 9			5	704	-701	9	173	45
			8	346	397							6	310	295			
0	-113	35	9	-125	147	0	-132	-27	0	-119	-19	7	-126	-57	H= 6 K= 10		
1	-113	-10	10	-143	114	1	210	-220	1	-120	67	8	-135	90			
2	137	-88	11	192	-266	2	-132	-27	2	-125	-91	9	328	-341	0	-139	-23
3	323	-313	12	242	288	3	-124	-97	3	-115	54	10	217	209	1	-132	20
4	119	112	13	340	-382	4	-134	10	4	-122	118	11	299	312	2	210	-219
5	171	-219	14	-140	-25	5	241	-230	5	-131	76				3	-133	-230
6	141	145	15	297	-277	6	127	64	6	-117	62	H= 5 K= 9			4	282	255
7	175	-158				7	-111	-89	7	-127	-88				5	-143	-23
8	178	181	H= 3 K= 6						8	-121	101	0	-130	40	6	-133	27
9	148	166				H= 3 K= 13			9	-123	112	1	138	116	7	-117	-71
10	-142	156	0	172	-167				10	-126	-57	2	277	256			
11	-116	36	1	123	-156	0	-137	20	11	-122	-54	3	116	9	H= 6 K= 11		
			2	258	269	1	-115	47				4	-125	2			
H= 2 K= 11			3	250	268	2	308	327	H= 4 K= 10			5	175	167	0	-142	22
			4	-112	-75	3	-125	-14				6	-142	102	1	-124	67
0	611	656	5	788	-785	4	-122	62				7	147	-159	2	235	270
1	-116	-124	6	-113	-82				0	313	314	8	-140	-90	3	-125	65
2	-116	-11	7	262	210	H= 4 K= 4			1	177	-182	9	152	40	4	-126	37
3	-105	16	8	-120	-23				2	-116	104	10	-130	-33			
4	439	467	9	-124	-49	0	367	365	3	-117	-198				H= 7 K= 7		
5	-119	149	10	332	360	1	100	0	4	226	244	H= 5 K= 10					
6	449	-422	11	-124	100	2	124	83	5	144	217				0	455	430
7	-122	-31	12	-128	85	3	-92	0	6	179	-226	0	381	395	1	-126	0
8	-124	8	13	-132	-76	4	270	-286	7	-132	-132	1	-128	-29	2	135	-51
9	153	-98	14	-136	-9	5	-103	0	8	185	188	2	531	515	3	-134	0
10	282	-253				6	522	504	9	-115	-117	3	-137	-113	4	376	-376
			H= 3 K= 7			7	-109	0	10	143	144	4	-130	-66	5	-131	0
H= 2 K= 12						8	170	180				5	-139	39	6	223	158
			0	261	-258	9	-117	0	H= 4 K= 11			6	-124	64	7	-118	0
0	-120	-4	1	185	-130	10	-127	24				7	-126	78	8	-137	70
1	-121	19	2	236	-240	11	-125	0	1	-130	23	8	259	-260	9	-123	0
2	-109	57	3	626	-643	12	257	229	2	-130	-31				10	-137	-24
3	-138	199	4	149	192	13	-140	0	3	-131	126	H= 5 K= 11					
4	-123	86	5	278	-301	14	-144	153	4	-140	120				H= 7 K= 8		
5	-124	6	6	188	167	15	-138	0	5	159	-84						
6	-113	12	7	-98	68				6	-135	11	0	318	-362	0	-132	40
7	-127	37	8	-119	166	H= 4 K= 5			7	-137	-8	1	300	279	1	-125	-48
8	-115	33	9	-113	-36				8	206	193	2	-134	83	2	141	-85
9	-107	-68	10	-116	-56	0	250	259				3	-125	-2	3	388	403
			11	-126	54	1	-101	-4	H= 4 K= 12			4	187	-157	4	296	225
H= 2 K= 13			12	209	222	2	153	128				5	286	225	5	228	256
			13	240	215	3	134	156	0	143	120	6	232	192	6	-130	79
0	-134	-86	14	-128	-21	4	158	172	1	-135	-14				7	234	182
1	-125	-86				5	141	105	2	-143	189	H= 5 K= 12			8	-134	114
2	-126	-13	H= 3 K= 8			6	-111	118	3	-144	36				9	173	-179
3	216	238				7	121	-109	4	-136	61	0	-138	36			
4	-115	56	0	197	178	8	-111	112	5	-132	126	1	-138	72	H= 7 K= 9		
5	190	196	1	125	-88	9	-121	-131	6	-117	41	2	145	-191			
6	-112	50	2	517	551	10	-125	14				3	141	121	0	-137	124
			3	-119	-3	11	-129	30	H= 5 K= 5						1	-130	98
H= 2 K= 14			4	129	67	12	-126	-19				H= 6 K= 6			2	-130	16
			5	131	-97	13	230	184	0	1444	1444				3	276	-246
0	-126	170	6	-125	-27	14	-141	-36	1	-100	0	0	837	814	4	-132	28
1	279	-287	7	146	199				2	101	98	1	-114	0	5	-133	-19
2	-122	67	8	338	-385	H= 4 K= 6			3	-108	0	2	-117	-57	6	-134	0
3	-119	92	9	-139	-71				4	1399	1677	3	-118	0	7	202	-206
			10	229	-239	0	-112	-32	5	-127	0	4	254	260			
H= 3 K= 3			11	148	137	1	139	170	6	781	-801	5	-127	0	H= 7 K= 10		
			12	263	-230	2	-113	101	7	-118	0	6	131	-113			
0	2270	2230	13	207	-225	3	-119	-83	8	128	-28	7	-126	0	H= 7 K= 9		
1	123	0				4	167	178	9	-117	0	8	194	196			
2	188	-263	H= 3 K= 9			5	-119	46	10	686	-679	9	-125	0	0	-135	-90
3	-81	0				6	301	301	11	-131	0	10	248	-302	1	-135	84
4	251	-101	0	-125	31	7	269	-241	12	-147	1	11	-138	0	2	-122	94
5	99	0	1	-118	34	8	261	257	13	-139	0	12	183	153	3	-122	-11
6	491	-420	2	-118	-14	9	-119	12	14	203	-241				4	-127	-69
7	-106	0	3	-119	-66	10	169	183									
8	179	166	4	-106	180	11	-126	44	H= 5 K= 6			H= 6 K= 7			H= 8 K= 8		
9	118	0	5	290	273	12	-130	-49									
10	694	-658	6	196	-196	13	150	125	0	-105	-176	0	-127	71	0	662	652
11	-120	0	7	-116	26	14	177	198	1	188	144	1	-128	-105	1	-129	0
12	162	158	8	-118	-25				2	-109	-76	2	332	302	2	-136	7
13	-135	0	9	112	63	H= 4 K= 7			3	373	353	3	-134	-68	3	-137	0
14	142	-158	10	-123	30				4	-109	39	4	163	88	4	441	440
15	-150	0	11	-114	-6	0	208	201	5	153	110	5	-127	-87	5	373	0
16	-128	-49	12	-121	66	1	532	551	6	221	249	6	-129	66	6	351	-284
						2	-114	159	7	-123	73	7	-124	-57	7	-134	0
H= 3 K= 4		H= 3 K= 10				3	-109	-21	8	164	111	8	224	-255			
						4	153	181	9	-129	-17	9	-129	105	H= 8 K= 9		
0	94	-119	0	-122	-66	5	-134	40	10	397	359	10	-139	-167			
1	201	-185	1	138	-130	6	259	-262	11	-128	31	11	-133	-37	0	-124	-43
2	254	270	2	276	-300	7	-130	57	12	239	128				1	-141	-73
3	-97	19	3	470	445	8	-127	88	13	-146	-56	H= 6 K= 8			2	-133	35
4	-100	64	4	140	139	9	-151	280							3	233	245
												0	-128	72	4	-127	36
												1	136	-70			

Table 3. *Interatomic distances in* $Pu_2Zn_{\sim 9}$

Standard deviations are about 0·01 Å for Pu–Zn distances and about 0·02 for Zn–Zn distances.

Pu(1)	Zn(1)	2	3·535 Å	Zn(5)	Pu(1)	1	3·278 Å
	Zn(5)	6	3·278		Pu(2)	1	3·125
	Zn(11)	6	2·865		Pu(4)	2	3·154
					Zn(1)	1	2·741
Pu(2)	Zn(3)	1	3·237		Zn(4)	2	3·469
	Zn(4)	2	3·106		Zn(5)	1	2·622
	Zn(4)	2	3·127		Zn(6)	2	2·914
	Zn(5)	1	3·125		Zn(11)	2	2·647
	Zn(6)	2	3·190				
	Zn(7)	2	3·190	Zn(6)	Pu(2)	2	3·190
	Zn(8)	2	3·138		Pu(3)	1	3·293
	Zn(9)	1	3·055		Pu(4)	1	3·286
	Zn(10)	1	3·231		Zn(4)	2	2·609
	Zn(11)	2	3·120		Zn(5)	2	2·914
	Zn(12)	2	3·840		Zn(6)	1	2·832
					Zn(7)	2	3·002
Pu(3)	Zn(2)	1	3·128		Zn(10)	1	2·593
	Zn(4)	4	3·092				
	Zn(6)	2	3·292	Zn(7)	Pu(2)	2	3·192
	Zn(7)	2	3·027		Pu(3)	1	3·027
	Zn(8)	2	3·132		Zn(3)	1	2·673
	Zn(9)	4	3·126		Zn(4)	2	3·001
	Zn(12)	2	3·684		Zn(6)	2	3·001
					Zn(7)	1	3·067
Pu(4)	Zn(1)	1	3·174		Zn(8)	1	2·933
	Zn(4)	4	3·332		Zn(10)	2	2·733
	Zn(5)	4	3·154		Zn(12)	1	2·546
	Zn(6)	2	3·286				
	Zn(9)	2	3·046	Zn(8)	Pu(2)	2	3·138 Å
	Zn(11)	4	3·877		Pu(3)	1	3·132
					Zn(2)	1	3·214
Zn(1)	Pu(1)	2	3·535 Å		Zn(3)	1	2·690
	Pu(4)	3	3·174		Zn(4)	2	3·089
	Zn(5)	6	2·741		Zn(7)	1	2·933
					Zn(8)	2	2·853
Zn(2)	Pu(3)	3	3·128		Zn(9)	2	2·577
	Zn(8)	6	3·214		Zn(12)	1	2·635
	Zn(9)	6	2·742				
				Zn(9)	Pu(2)	1	3·055
Zn(3)	Pu(2)	3	3·237		Pu(3)	2	3·126
	Zn(7)	3	2·673		Pu(4)	1	3·046
	Zn(8)	3	2·690		Zn(2)	1	2·742
	Zn(10)	3	2·688		Zn(4)	2	2·669
					Zn(8)	2	2·577
Zn(4)	Pu(2)	1	3·106		Zn(9)	1	2·623
	Pu(2)	1	3·127				
	Pu(3)	1	3·092	Zn(10)	Pu(2)	2	3·231
	Pu(4)	1	3·332		Zn(3)	2	2·688
	Zn(4)	1	2·963		Zn(6)	2	2·593
	Zn(5)	1	3·469		Zn(7)	4	2·733
	Zn(6)	1	2·609		Zn(10)	2	2·716
	Zn(7)	1	3·001				
	Zn(8)	1	3·089	Zn(11)	Pu(1)	1	2·865
	Zn(9)	1	2·669		Pu(2)	2	3·120
	Zn(11)	1	2·636		Pu(4)	2	3·876
	Zn(12)	1	2·628		Zn(4)	2	2·636
					Zn(5)	2	2·647
					Zn(11)	2	2·865
				Zn(12)	Pu(2)	4	3·830
					Pu(3)	2	3·684
					Zn(4)	4	2·628
					Zn(7)	2	2·546
					Zn(8)	2	2·635

where K is a scale factor, g is an extinction parameter (Zachariasen, 1963), Lp is the Lorentz and polarization factor and F_c is the ordinary calculated structure factor. Anisotropic thermal parameters were in the form

$$\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})] .$$

Scattering factors were taken from Cromer & Waber (1965) and were modified by the real parts of the anomalous dispersion terms from Cromer (1965).

A three-dimensional Patterson function was calculated for the subcell and the approximate locations of 24 Pu atoms were found. Several Fourier and least-squares iterations led to a structure consisting of 26 Pu atoms and 116 Zn atoms in the subcell. R was 15·1% at this stage of refinement. All atoms were then given anisotropic thermal parameters and R was reduced to 10·3%. The final parameters are listed in Table 1 and the observed and calculated structure factors in Table 2. At the last cycle the ratio $\Delta\xi_i/\sigma\xi_i \leq 0{\cdot}06$ for all parameters ξ and the average value was $\sim 0{\cdot}001$. The value of $\sigma(\varrho)$ was 1·6 e.Å^{-3}. Difference Fourier maps showed several peaks of 4 to 5 e.Å^{-3}, but attempts to place an additional atom or partial atom at any of these locations have thus far resulted in impossibly large thermal parameters for the additional atom, even though many of the locations are in sufficiently open regions to accommodate another atom after small shifts of surrounding atoms. However, since the present analysis is known to be an approximation to the true structure, it is not surprising to find significant features in the difference Fourier.

Certain of the atoms, namely Pu(4), Zn(11) and Zn(12), have large anisotropic thermal parameters. These atoms were split into two half atoms somewhat off the symmetry elements and given isotropic thermal parameters, the remaining atoms being retained as anisotropic. This refinement proceeded to the same R, 10·3%. Hence, it is not possible to distinguish between these models, and for purposes of discussion we will use the ordered anisotropic model.

Discussion

Table 3 lists the interatomic distances between neighboring atoms. Atoms are defined as neighbors if the midpoint between the two atoms is closer to these atoms than to any other. Standard deviations are about 0·01 Å for Pu–Zn distances and about 0·02 Å for Zn–Zn distances and were computed with the use of the full inverse matrix and include lattice constant errors. There are no other distances less than 4·0 Å. Table 4 gives the size and orientation of the thermal ellipsoids.

Table 4. *Thermal ellipsoids for* $Pu_2Zn_{\sim 9}$

α, β and γ are the angles which the ellipsoid axes make with the real lattice axes a, b, and c.
Standard deviations, in parentheses, apply to the rightmost digit.

	B_i	α	β	γ
Pu(1)	2·4 (4) Å^2	0°	120°	90°
	2·4 (4)	90	30	90
	4·2 (7)	90	90	0
Pu(2)	1·9 (2)	46 (7)	134 (7)	127 (10)
	1·9 (2)	60	60	90
	1·1 (2)	58 (8)	122 (8)	37 (10)
Pu(3)	1·7 (3)	30	150	90
	1·8 (3)	60	60	90
	1·7 (2)	90	90	0
Pu(4)	1·2 (4)	30	150	90
	1·9 (4)	60	60	90
	13·8 (9)	90	90	0
Zn(1)	2·0 (11)	0	120	90
	2·0 (11)	90	30	90
	2·3 (16)	90	90	0
Zn(2)	0	0	120	90
	0	90	30	90
	4·0 (20)	90	90	0
Zn(3)	0·8 (5)	0	120	90
	0·8 (5)	90	30	90
	0	90	90	0
Zn(4)	5·4 (7)	26 (9)	128 (7)	113 (6)
	−0·1 (4)	100 (5)	48 (5)	136 (6)
	2·5 (5)	66 (9)	66 (7)	55 (9)

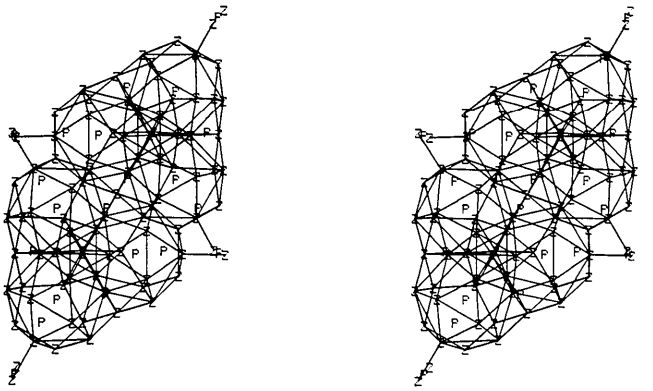

Fig. 1. The unit-cell contents of $Pu_2Zn_{\sim 9}$ lying between the mirrors at $z=\frac{1}{4}$ and $\frac{3}{4}$. An orthogonal coordinate system is defined with X parallel to **a**, Y parallel to **b*** and Z parallel to **c**. The direction of view is defined by the vector [001]. The letters P and Z are plotted at the Pu and Zn locations respectively.

Table 4 (*cont.*)

	B_i	α	β	γ
Zn(5)	0·7 (7)	34 (5)	146 (5)	106 (11)
	3·4 (9)	60	60	90
	3·7 (8)	76 (9)	104 (9)	16 (11)
Zn(6)	2·0 (6)	38 (22)	158 (22)	90
	0·7 (6)	52 (22)	68 (22)	90
	1·5 (5)	90	90	0
Zn(7)	2·1 (6)	53 (9)	127 (9)	136 (12)
	2·1 (7)	60	60	90
	−0·0 (5)	52 (9)	128 (9)	46 (12)
Zn(8)	0·7 (5)	30 (2)	150 (2)	92 (36)
	1·3 (6)	60	60	90
	1·5 (5)	89 (32)	92 (32)	2 (34)
Zn(9)	2·0 (7)	33 (8)	147 (8)	75 (20)
	1·2 (6)	60	60	90
	0·6 (5)	103 (17)	77 (17)	15 (20)
Zn(10)	1·9 (10)	30	150	90
	2·1 (10)	60	60	90
	0·6 (7)	90	90	0
Zn(11)	3·0 (11)	0	120	90
	2·2 (9)	90	45 (3)	125 (4)
	19·2 (28)	90	60 (3)	35 (4)
Zn(12)	7·8 (21)	0	120	90
	0·5 (10)	90	31 (2)	96 (12)
	5·8 (15)	90	85 (10)	6 (12)

Fig. 1 is a stereo drawing of the unit-cell contents lying between the mirrors at $z=\frac{1}{4}$ and $\frac{3}{4}$.

The Pu atoms have Zn atom neighbors exclusively. With the exception of the 6 Zn(11) neighbors of Pu(1) at 2·87 Å all Pu–Zn distances are longer than the sum of the metallic radii, which is about 2·9 to 3·0 Å depending on the value chosen for Pu. The coordination polyhedra about the Pu atoms are rather large, particularly the one for Pu(4). Figs. 2–5 are stereo drawings of the four Pu coordination polyhedra. Pu(1) has 14 neighbors arranged to form a polyhedron with six pentagonal faces and six triangular faces. Each pentagonal face is shared with a Pu(4) polyhedron. Pu(2), in Fig. 3, has 18 neighbors arranged in two pentagons on either side and a heptagon around the middle. One of the end pentagons is closed by the 18th atom. The other pentagon is shared with the Pu(4) polyhedron.

Fig. 4 shows Pu(3) with its 17 neighbors. These neighbors form pentagons on either side and a heptagon in the middle. As with the other polyhedra, the pentagons are shared with Pu(4) polyhedra. The Pu(4) polyhedron is shown in Fig. 5. There are 17 neighbors forming a polyhedron which is rather elongated in the z direction. There are six pentagonal faces and three triangular faces. The pentagonal faces are shared, two each, with the other three kinds of Pu polyhedra.

The Zn atoms have a variety of polyhedra with the number of neighbors ranging from 10 to 15. Zn(3), Zn(6) and Zn(10) have 12 neighbors arranged in distorted icosahedra. Zn(2) has 15 neighbors which form the triangulated polyhedron of Frank & Kasper (1958). The Zn(1) polyhedron can be described as a trigonal prism with atoms added at each of the five faces. Zn(11) is topologically similar to Zn(1) but rather distorted. Zn(4), which is the only atom in a general position, has 12 neighbors forming an irregular polyhedron. Zn(5) has a rather irregular polyhedron which with a little imagination can be described as distorted hexagonal close packed. Zn(7) and Zn(8), with 13 neighbors have the same point symmetry and the polyhedra

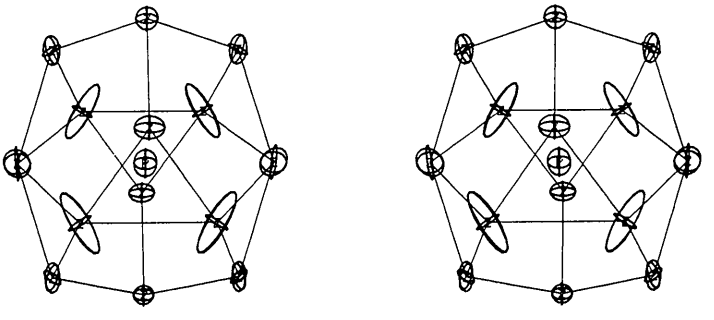

Fig. 2. The Pu(1) polyhedron as viewed along the vector [0, 0·866, 0·5].

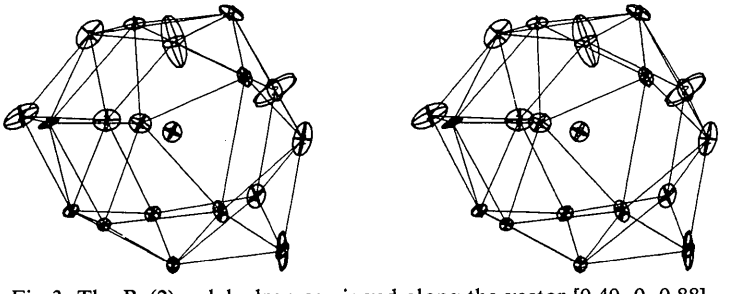

Fig. 3. The Pu(2) polyhedron as viewed along the vector [0·49, 0, 0·88].

are topologically similar. The Zn(7) polyhedron can be described as a belt of five atoms on one side and a belt of six on the other with an atom capping each belt. In the Zn(8) polyhedron the six-atom belt is more puckered than in the Zn(7) polyhedron. The Zn(9) polyhedron is a distorted Archimedes antiprism with atoms capping each end. The surroundings of Zn(12) are similar to a body-centered cubic arrangement, there being 8 Zn atoms appoximately at the corners of a cube and 6 Pu atoms displaced from the cube faces.

The elongated Pu(4) polyhedron and the large thermal parameters of Pu(4) and Zn(11) suggest a possible mechanism for creation of the present superlattice and the microphases in the Ce–Cd system. An atom could be inserted between the Pu(4) atom and the pair of Zn(11) atoms, pushing the Zn(11) atoms in the direction of the major axis of the thermal ellipsoid and displacing the Pu(4) atom toward the Zn(11) atoms at the other end of the polyhedron. A small displacement of Zn(4) and Zn(5) would also be required. These atoms have their major ellipsoid axis oriented so as to suggest that this displacement is occurring.

Many trial and error attempts were made to solve the structure of the true unit cell but without success. Most of these trials assumed space group $P6_322$. However, as mentioned previously, the probability of twinning is high and the true unit cell may have Laue symmetry lower than $6/mmm$. Because of the uncertain symmetry we do not include in this report any data on the large unit cell. We will be glad to supply these data on request.

We do not intend to investigate the present compound any further. However, we hope in the future to investigate this phase in other systems.

Note added in proof:– Wang (1967) has recently published some work on $Gd_{13}Zn_{58}$. He proposes a structure in space group $P6_3mc$ although the structure is very nearly centric. If 0·265 is subtracted from all z coordinates in the proposed structure for $Gd_{13}Zn_{58}$, the result is quite similar to that which we give in the present paper.

All calculations were done with an IBM 7094 using programs written by Larson, Cromer & Roof (1963–1965). The stereo drawings were made with an SC-4020 microfilm plotter.

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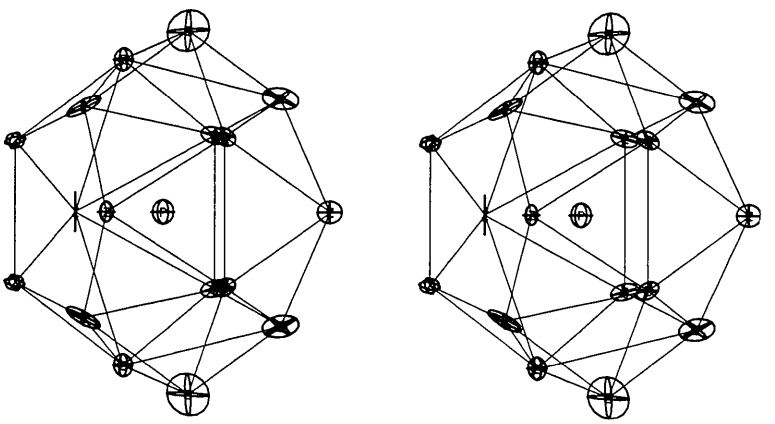

Fig. 4. The Pu(3) polyhedron as viewed along the vector [100].

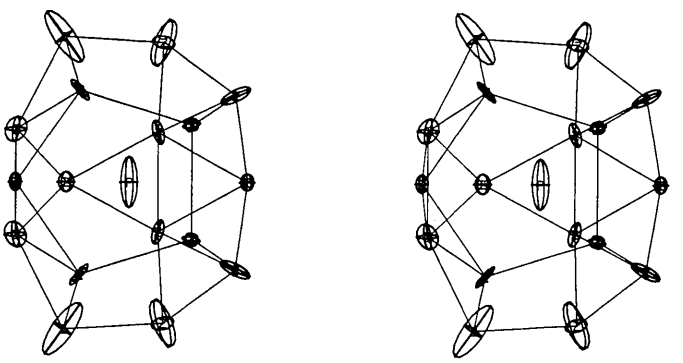

Fig. 5. The Pu(4) polyhedron as viewed along the vector [−0·5, 0·866, 0].

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The Crystal Structure of Ti_2S*

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The crystal structure of dititanium sulfide, Ti_2S, has been determined from single-crystal X-ray diffraction data. The compound crystallizes in the orthorhombic system, space group *Pnnm*, with unit-cell dimensions $a=11{\cdot}35$, $b=14{\cdot}06$, $c=3{\cdot}32$ Å. The unit cell contains 12 formula units. All atoms are located in layers separated by $c/2$. Refinement of the structure was performed by least-squares treatment of x and y positional parameters and isotropic temperature factor coefficients. The sulfur bonding is interpreted with bond order calculations and is shown to be consistent with sulfur atoms utilizing d orbitals to form either electron deficient bonds to at least seven metal atoms or directional electron deficient bonds to six metals with trigonal prismatic symmetry.

Introduction

The titanium–sulfur system has received much attention since a systematic study by Biltz, Ehrlich & Meisel (1937). The stoichiometries of the condensed phases in this system are still not thoroughly understood. In the lower sulfide region ($M/S \geq 1$) especially, the situation is unclear owing to a lack of information on the stability and homogeneity ranges of the reported phases.

Filonenko & Kydryavtsev (1953) described a hexagonal 'τ-Ti_2S' phase which later was shown by Kudielka & Rohde (1960) to be a phase with the ideal composition Ti_2CS. Hägg & Schönberg (1954) suggested the existence of a stable Ti_2S to explain powder diffraction data which were obtained from their subsulfide preparations. Abendroth & Schlechten (1959) reported some of the same diffraction lines as did Hägg & Schönberg, although they ascribed the other lines present in their subsulfide pattern to the 'Ti_5S_4' phase.

In a review of transition metal sulfides, Jellinek (1963) suggested that the additional lines in Hägg & Schönberg's and Abendroth & Schlechten's patterns were due to impurities formed by reaction of the metal with the quartz preparative tubes. Work on the extent of impurities in lower titanium sulfides was also performed by Bartrum (1958) and by Hahn & Ness (1959).

Franzen & Gilles (1965), while studying the vaporization behavior of TiS, prepared a subsulfide, the further characterization of which was undertaken by Stone (1963).

Stone obtained accurate lattice parameters by a least-squares fit of Guinier powder diffraction lines. His values were $a=11{\cdot}35$, $b=14{\cdot}06$, $c=3{\cdot}32$ Å. The parameters obtained from single-crystal diffraction patterns in the work reported here are in complete agreement with these values. Stone also determined the space group symmetry and concluded that two space groups were possible, namely *Pnn*2 and *Pnnm*, in agreement with our findings as discussed below. Density determinations performed by Stone, employing a buoyancy method with two liquids and a pycnometer method with the same liquids, yielded an average density of $4{\cdot}80$ g.cm^{-3}, corresponding to $11{\cdot}97$ Ti_2S units per unit cell. It was reported by Stone that combustion analysis yielded $S/Ti=0{\cdot}498$.

The work reported here was conducted for the purpose of establishing the existence and structure of the Ti_2S phase.

Experimental

The dititanium sulfide samples were prepared by annealing pellets composed of equimolar quantities of titanium monosulfide and titanium filings. The titanium monosulfide samples were prepared by heating mixtures of titanium filings and sulfur in sealed Vycor tubes

* Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission. Contribution no. 1967.