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The crystal structure of Th_3Pd_5 and Th_3Pt_5.

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The crystal structures of several intermetallic compounds of thorium with palladium and platinum have been reported recently, that of Th_2Pd(C16) by Ferro (1961), of $ThPd_3(DO_{24})$ by Dwight (1961), and of $ThPd_4(LI_2)$ by Thomson (1962*a*); the structures of $Th_7Pt_3(D10_2)$ and ThPt(B_f) were given by Thomson (1961, 1962*b*). The crystal structures of the compounds Th_3Pd_5 and Th_3Pt_5 are described in the present paper.

The alloys were prepared by arc-melting the component metals into 1-gram buttons in a zirconium-gettered argon atmosphere. As the alloys were brittle, powders for X-ray studies were prepared by crushing in air and gave very sharp X-ray patterns without a strain-relieving anneal. Powder patterns were obtained with a Guinier-type focusing camera using copper radiation and a quartz monochromator ($\lambda K\alpha_1 = 1{\cdot}54050$ Å) and the line intensities were estimated visually.

Table 1. *Comparison of observed and calculated* $\sin^2\theta$ *values and line intensities for* Th_3Pd_5

hkl	$\sin^2\theta_o$	$\sin^2\theta_c$	I_o	I_c
100	—	0·0155	—	< 1
001	—	0·0390	—	8
110	0·0464	0·0464	*s*	252
101	0·0543	0·0545	*vvw*	14
200	0·0617	0·0619	*vvw*	13
111	0·0854	0·0855	*vs*	1000
201	0·1009	0·1009	*w*	77
210	0·1083	0·1084	*m*	144
300	0·1394	0·1393	*s*	226
211	0·1475	0·1474	*mw*	90
002	0·1561	0·1561	*m*	124
102	—	0·1716	—	< 1
301	0·1783	0·1783	*mw*	83
220	0·1857	0·1858	*m*	108
310	—	0·2012	—	10
112	0·2025	0·2025	*mw*	67
202	—	0·2180	—	3
221	0·2247	0·2248	*m*	94
311	0·2404	0·2403	*vvw*	22
400	—	0·2477	—	< 1
212	0·2645	0·2644	*w*	68
401	—	0·2867	—	16
320	—	0·2941	—	7
302	0·2953	0·2954	*m*	131
410	0·3254	0·3251	*vw*	50
321	0·3334	0·3333	*vw*	30
222	0·3418	0·3418	*w*	77
003	—	0·3512	—	< 1
312	—	0·3573	—	7
411	0·3641	0·3641	*ms*	190
103	—	0·3667	—	< 1
500	—	0·3870	—	8
113	0·3976	0·3976	*mw*	85
402	—	0·4038	—	< 1
203	—	0·4131	—	8
330	0·4182	0·4180	*vvw*	27

vs = very strong, *s* = strong, *ms* = medium strong, *m* = medium, *mw* = medium weak, *w* = weak, *vw* = very weak, *vvw* = extremely weak.

The film of the alloy of 63 at.% palladium was indexed as hexagonal with

$$a = 7{\cdot}149 \pm 0{\cdot}003,\quad c = 3{\cdot}899 \pm 0{\cdot}002 \text{ Å},\quad c/a = 0{\cdot}545;$$

observed and calculated values of $\sin^2\theta$ are given in Table 1. No systematic extinctions were observed. The volume of the unit cell suggested that the compound was Th_3Pd_5 with one unit of Th_3Pd_5 per unit cell; this gave a calculated density of 11·84 g.cm.$^{-3}$. Examination of alloys of neighbouring compositions indicated that Th_3Pd_5 has only a narrow range of homogeneity and that it is in equilibrium with $ThPd_3$.

Visual examination of a focusing-camera film of an alloy containing 63 at.% platinum suggested that Th_3Pt_5 was isostructural with Th_3Pd_5 and $\sin^2\theta$ values corresponding to

$$a = 7{\cdot}162 \pm 0{\cdot}003,\quad c = 3{\cdot}908 \pm 0{\cdot}002 \text{ Å},\quad c/a = 0{\cdot}546$$

gave good agreement with the observed values.

For Th_3Pd_5 a structure with:

$2\,Pd_I$ in $\frac{1}{3}, \frac{2}{3}, 0;\ \frac{2}{3}, \frac{1}{3}, 0$
$3\,Pd_{II}$ in $x_{Pd}, 0, 0;\ 0, x_{Pd}, 0;\ \bar{x}_{Pd}, \bar{x}_{Pd}, 0;\ x_{Pd} = 0{\cdot}75$
$3\,Th$ in $x_{Th}, 0, \frac{1}{2};\ 0, x_{Th}, \frac{1}{2};\ \bar{x}_{Th}, \bar{x}_{Th}, \frac{1}{2};\ x_{Th} = 0{\cdot}33$

gave a rough fit to the observed intensities. The atomic parameters were refined using the A.E.R.E. Ferranti 'Mercury' computer; the refined parameters $x_{Pd} = 0{\cdot}780 \pm 0{\cdot}002$ and $x_{Th} = 0{\cdot}350 \pm 0{\cdot}002$ gave good agreement between observed and calculated intensities as shown in Table 1. The highest-symmetry space group in which these atomic positions are possible is D_{3h}^3-$P\bar{6}2m$. A search of the literature has failed to reveal any other intermetallic compounds with this structure.

Interatomic distances for Th_3Pd_5 were calculated to be as follows:

Pd_I–3 Pd_{II}	2·87 Å	Pd_{II}–2 Pd_{II}	2·72 Å	Th–4 Pd_{II}	2·93 Å
–6 Th	3·03	–2 Pd_I	2·87	–4 Pd_I	3·03
		–4 Th	2·93	–2 Pd_{II}	3·64
		–2 Th	3·64	–2 Th	3·90
				–4 Th	4·03

The coordination of 16 around the thorium atom in Th_3Pd_5 is in general agreement with the suggestion by Frank & Kasper (1958, 1959) and Kripyakevich (1960) that a high coordination around the larger atoms in intermetallic compounds might contribute to the stability of certain structures.

Table 2. *Closest neighbours in* Th–Pd *compounds*

	Compound	Th–Th	Th–Pd	Pd–Pd
Th_3Pd_5		3·899 Å	2·932 Å	2·725 Å
$ThPd_3$	(Thorium limit)	4·178	2·930	2·930
	(Palladium limit)	4·149	2·923	2·923
$ThPd_4$	(Thorium limit)	4·126	2·918	2·918
	(Palladium limit)	4·110	2·905	2·905

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In a recent discussion of the interatomic distances in $ThPd_3$ and $ThPd_4$, both of which have a range of composition of a few per cent (Thomson, 1962*a*), it was pointed out that the closest Th–Pd distance increased with increasing thorium composition and, as shown in Table 2, this trend is continued in the neighbouring compound Th_3Pd_5. The Th–Th and Pd–Pd distances do not follow any trend. Given that the atomic radii (for C.N. 12) in the pure metals are 1·37 and 1·80 Å for palladium and thorium respectively, there is a considerable contraction in the Th–Pd distance in all three compounds.

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Preliminary X-ray study on the dioxane addition compounds of hydrated rare earth perchlorates.

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Dioxane addition compounds of hydrated rare-earth perchlorates have been prepared for the first time by Vicentini, Perrier & Giesbrecht (1961), and their crystallographic properties are now described in this paper. Their general chemical formula is $M(ClO_4)_3 . 9\,H_2O . 4\,C_4H_8O_2$, with $M =$ La, Ce, Pr, Nd, Sm. The five compounds form an isomorphous series.

The substances are usually both powdery and very hygroscopic, and so no good crystals were available for use of X-ray single-crystal techniques. Attempts to grow thicker specimens were ineffective.

Under the microscope, the crystals are biaxial with parallel extinction. The $2V$ angles were measured with the universal stage and the indices of refraction were determined with the petrographic microscope by the immersion method. The figures in Table 1 are only approximate, on account of the unstable character of the substances.

The unit-cell dimensions (Table 2) were computed by Ito's procedure (1950), applied to powder photographs obtained in a 114·6 mm Buerger powder camera. The assignment of indices (Table 3) corroborated the orthorhombic system, already suspected from the optical data.

The pycnometer method was used for determination of densities, with dioxane as the immersion liquid. Random errors may occur in the second decimal place, due to the probable absorption of dioxane while the density determinations were carried out.

The number of formulas per unit cell is approximately 6. No systematic absences were observed, and thus three alternative space groups are possible: *Pmmm*, *P*2*mm* and *P*222.

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Table 1. *Optical constants*

	La-compound	Ce-compound	Pr-compound	Nd-compound	Sm-compound
N_X (obs.)	1·454	1·455	1·453	1·458	1·460
N_Y (obs.)	1·457	1·458	1·456	1·461	1·464
N_Z (calc.)	1·464	1·465	1·464	1·469	1·473
N_Z-N_X (calc.)	0·010	0·010	0·011	0·011	0·013
$2V_Z$ (obs.)	65 ± 2°	68 ± 2°	63 ± 2°	64 ± 2°	67 ± 2°

Table 2. *Unit cell dimensions, cell volumes and densities*

	a_0	b_0	c_0	V	d (obs.)	d (calc.)
La-compound	16·07 Å	17·87 Å	19·50 Å	5·600 Å³	1·69 g.cm⁻³	1·69 g.cm⁻³
Ce-compound	16·05	17·70	19·39	5·508	—	1·72
Pr-compound	15·83	17·76	19·35	5·440	1·71	1·75
Nd-compound	15·81	17·76	19·31	5·422	—	1·76
Sm-compound	15·85	17·56	19·24	5·355	1·70	1·79