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**The crystal structure of ThPt and some related compounds.** By JEAN R. THOMSON,\* *Department of Metallurgy, Imperial College of Science and Technology, London, S. W. 7, England.*

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An investigation of the constitution of alloys of thorium and the platinum metals is in progress and the crystal structures of five intermetallic compounds of the type  $\text{Th}_7\text{X}_3$  have been reported (Thomson, 1961) the structure of  $\text{Th}_7\text{Rh}_3$  has since been confirmed by Ferro & Rambaldi (1961). The structures of ThRu and ThIr were recently reported briefly (Thomson, 1962) and the structures of ThPt and ThRh are the subject of the present paper.

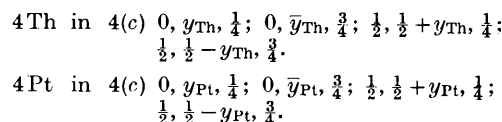
The alloys were prepared as one g. buttons by arc-melting the component metals in a zirconium-gettered argon atmosphere. All samples were brittle and powders for X-rays studies were prepared by crushing in air;

powder patterns were obtained with a Guinier-type focusing camera using monochromatized copper radiation ( $\lambda K\alpha_1 = 1.54050 \text{ \AA}$ ) and the line intensities were estimated visually.

The X-ray pattern of the alloy of 50 at.% platinum was indexed on the basis of an orthorhombic unit cell

$$a = 3.900 \pm 0.003, \quad b = 11.09 \pm 0.01, \quad c = 4.454 \pm 0.003 \text{ \AA}$$

and observed and calculated values of  $\sin^2 \theta$  are shown in Table 1. No  $hkl$  reflections were observed unless  $h+k$  was even and  $h0l$  lines were present only when  $l$  was even. The lattice parameters and systematic extinctions suggested that ThPt was isostructural with ThCo (Florio, 1956), CrB structure, space group  $D_{2h}^{14}Cmcm$ . The atomic positions are as follows:



Line intensities calculated on the basis of this structure with  $y_{\text{Th}} = 0.140 \pm 0.002$  and  $y_{\text{Pt}} = 0.410 \pm 0.004$  gave good agreement with the observed intensities as shown in Table 1. With these atomic positions, the following interatomic distances were obtained:

Th-1Pt	2.99 \AA	Pt-2Pt	2.99 \AA
4Pt	3.01	1Th	2.99
2Pt	3.21	4Th	3.01
2Th	3.82	2Th	3.21
4Th	3.84		
2Th	3.90		
2Th	4.45		

ThRh was found to be isostructural with ThPt with

$$a = 3.866 \pm 0.003, \quad b = 11.24 \pm 0.01, \quad c = 4.220 \pm 0.003 \text{ \AA}.$$

$$y_{\text{Th}} = 0.140 \pm 0.004 \quad \text{and} \quad y_{\text{Rh}} = 0.410 \pm 0.004.$$

Pearson (1958) stated that by choosing the appropriate axes and origins the CrB( $B_f$ ) and CaSi( $B_c$ ) structures become identical and Kripyakevich (1962) has recently pointed out that the TII (yellow modification) structure is similar. Isotypes of ThPt therefore include ThRu, ThIr, ThCo, ThAl (Braun, 1955), PuNi (Cromer, 1959), CeNi (Finney, 1961), DyGa (Baenziger, 1961) and HfAl (Edshammar, 1961).

In ThPt the Pt(X) atoms form zig-zag chains through the structure and the X-X distances within these chains are shown in Table 2 together with the lattice parameters and the shortest Th-X and Th-Th distances. Similar data are included for the isostructural compounds of thorium. There is no ThX compound in the system Th-Os and ThPd has a different crystal structure.

Apart from ThAl, the X-X distances show an increase of approximately 10% and the Th-X distances a decrease of about 7% compared with those obtained by addition of Pauling's values of the atomic radii for C.N. 12 (Pauling, 1956). During an investigation of the crystal

Table 1. *Crystallographic data for ThPt*

<i>hkl</i>	$\sin^2 \theta$ (obs.)	$\sin^2 \theta$ (calc.)	<i>I</i> (obs.)	<i>I</i> (calc.)
020	0.0193	0.0193	<i>vvw</i>	24
110	—	0.0438	—	5
021	0.0492	0.0492	<i>vvw</i>	21
111	0.0736	0.0737	<i>vs</i>	1000
040	0.0769	0.0771	<i>ms</i>	340
130	0.0823	0.0824	<i>mw</i>	168
041	0.1068	0.1070	<i>mw</i>	205
131	0.1122	0.1123	<i>s</i>	644
002	0.1196	0.1196	<i>m</i>	295
022	—	0.1389	—	4
200	0.1558	0.1560	<i>mw</i>	202
150	0.1594	0.1595	<i>vvw</i>	28
112	—	0.1634	—	1
060	—	0.1732	—	4
220	—	0.1753	—	3
151	0.1895	0.1894	<i>vw</i>	83
042	0.1967	0.1967	<i>mw</i>	179
132	0.2018	0.2020	<i>w</i>	92
061	0.2033	0.2034	<i>vvw</i>	32
221	—	0.2052	—	7
240	0.2331	0.2331	<i>w</i>	139
241	0.2630	0.2630	<i>w</i>	112
170	—	0.2752	—	120
202	0.2756	{ 0.2756	<i>m</i>	{ 167
152	—	0.2791	—	23
023	—	0.2884	—	2
062	—	0.2931	—	4
222	—	0.2949	—	2
171	0.3050	0.3051	<i>vvw</i>	47
080	—	0.3085	—	9
113	0.3130	0.3129	<i>w</i>	118
260	—	0.3295	—	3
081	0.3381	0.3384	<i>vw</i>	83
043	0.3461	0.3462	<i>vvw</i>	36
133	0.3513	0.3515	<i>w</i>	116
242	0.3529	0.3527	<i>w</i>	147
310	—	0.3558	—	2
261	—	0.3594	—	27
311	0.3858	0.3857	<i>vw</i>	87
330	—	0.3944	—	16
172	0.3946	{ 0.3948	<i>w</i>	{ 135

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

\* Formerly J. R. Murray.

Table 2. Structural data for ThX compounds having the CrB structure

ThX	'a' (Å)	'b' (Å)	'c' (Å)	$y_{Th}$	$y_x$	X-X		Th-X		Th-Th in ThX
						in ThX	for C.N.12	in ThX	for C.N.12	
ThCo	3.74	10.88	4.16	0.136	0.416	2.77	2.50	2.86	3.05	3.62
ThRu	3.878	11.29	4.071	0.144	0.410	2.86	2.67	2.87	3.13	3.75
ThRh	3.866	11.24	4.220	0.140	0.410	2.92	2.68	2.92	3.14	3.78
ThIr	3.894	11.13	4.266	0.140	0.410	2.93	2.70	2.94	3.15	3.79
ThPt	3.900	11.09	4.454	0.140	0.410	2.99	2.77	2.99	3.18	3.82
ThAl	4.42	11.45	4.19	0.147	0.443	2.46	2.85	3.22	3.22	3.85

structures of ThAl<sub>3</sub> and Th<sub>3</sub>Al<sub>2</sub>, the present author (Murray, 1955) found that since the scattering powers of thorium and aluminium differ by a factor of about 8, it was not possible to determine the aluminium atomic parameters in those compounds from intensity calculations. Accordingly, the aluminium parameters suggested for ThAl<sub>3</sub> and Th<sub>3</sub>Al<sub>2</sub> were derived from geometrical considerations. In a recent paper, van Vucht (1961) has confirmed that his aluminium parameter for ThAl was also derived from geometrical considerations on the assumption that each large (Th) atom had 6 equidistant small (Al) neighbours. Since this condition is not satisfied in several other compounds with this structure (e.g. ThCo, PuNi, CeNi, DyGa and HfAl) it may not be necessary in ThAl. A small decrease in the Al parameter would lead to an increase in Al-Al and a rather smaller decrease in Th-Al.

In a recent survey of borides and silicides of the transition metals, Aronsson (1960) has pointed out that the occurrence of the CrB structure depends to a rather large extent on a favourable radius ratio  $r_x/r_M \cong 0.7$ . He also suggested that, since the same structure is found among intermetallic compounds, 'electronic' factors may not be of primary importance in its formation. In the present series of compounds, the radius ratio varies between 0.69 for ThCo to 0.79 for ThAl in general agreement with Aronsson's observations, but the decreased Th-X distances suggest that there may be appreciable Th-X interaction.

Frank & Kasper (1958, 1959) and Kripyakevich (1960) have noted that there is often a high coordination around the larger atoms in intermetallic compounds and they suggested that this might contribute to the stability of certain structures. In the present ThX series the coordination around the larger, thorium atom is  $(4 + 2 + 1)X +$

$(4 + 2 + 2 + 2)Th = 17$  whilst that around the smaller, X, atom is  $2X + (4 + 2 + 1)Th = 9$  in support of this suggestion.

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### The crystal structure of Ti<sub>2</sub>Ni. (A correction). By G. A. YURKO, J. W. BARTON and J. GORDON PARR, Department of Mining and Metallurgy, University of Alberta, Edmonton, Alberta, Canada

Dr. Linus Pauling has written to us to point out an anomaly in Table 2 of the paper by G. A. Yurko, J. W. Barton, and J. Gordon Parr (1959).

Only two titanium positions are required (as the paper itself stated), and the table should be amended to include:

Atom	Bond	Num. of bonds	Distance
Ti(48f)	Ti-Ni	2	2.57 ± 0.05 Å
	Ti-Ni	2	2.91 ± 0.05
	Ti-Ti	2	2.93 ± 0.02
	Ti-Ti	4	2.95 ± 0.05
	Ti-Ti	4	2.91 ± 0.05
		<u>4</u>	

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Atom	Bond	Num. of bonds	Distance
Ti(16c)	Ti-Ni	6	2.49 ± 0.02 Å
	Ti-Ti	6	2.93 ± 0.00
		<u>12</u>	

Some changes relating to coordination numbers mentioned in the discussion must therefore be made, but the rest of the paper is unaffected. We do, however, apologize for our error, and are grateful to Dr. Pauling for drawing our attention to it.

J. Gordon Parr

### Reference

- YURKO, G. A., BARTON, J. W. & PARR, J. GORDON (1959). *Acta Cryst.* **12**, 909.