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The crystal structure of ThPd.

By J. R. Thomson,* *Department of Metallurgy, Imperial College of Science and Technology, London S.W. 7, England*

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The Th–Pd binary system has been investigated recently (Thomson, 1963*a*) and mention was made of an intermetallic compound which was observed at approximately 50 at.% palladium. The crystal structure of this compound is the subject of the present paper.

The alloy samples were prepared as 1-g buttons by arc-melting the component metals in a zirconium-gettered argon atmosphere. These alloys were brittle and powders for X-ray studies were prepared by crushing under carbon tetrachloride. X-ray powder patterns were obtained with a Guinier-type focusing camera, copper radiation and a quartz monochromator ($\lambda K\alpha_1 = 1{\cdot}54050$ Å) being used, and the line intensities were estimated visually.

Table 1. *Crystallographic data for* ThPd

hkl	$\sin^2\theta$ (obs)	$\sin^2\theta$ (calc)	*I* (obs)	*I* (calc)
101	—	0·0286	—	3
200	0·0454	0·0452	*w*	33
011		0·0457		236
111	0·0568	0·0570	*s*	1000
201	0·0627	0·0625	*vw*	224
002	—	0·0692	—	< 1
210	0·0733	0·0736	*s*	983
102	0·0806	0·0805	*s*	948
211	0·0908	0·0909	*s*	944
112	0·1089	0·1089	*s*	970
020	0·1139	0·1136	*m*	642
202	—	0·1144	—	1
301	0·1185	0·1189	*m*	512
121	—	0·1422	—	< 1
212	—	0·1428	—	< 1
311	—	0·1473	—	99
220	—	0·1588	—	16
103	—	0·1670	—	1
302	—	0·1708	—	< 1
221	—	0·1761	—	109
400	—	0·1806	—	3
022	—	0·1828	—	< 1
013	—	0·1841	—	52
122	0·1942	0·1941	*m*	520
113	—	0·1954	—	163
401	0·1976	0·1979	*vw*	216
312	—	0·1992	—	172
203	—	0·2009	—	49
410	—	0·2090	—	106
411	—	0·2263	—	55
222	—	0·2280	—	< 1
213	0·2297	0·2293	*vw*	201
321	0·2326	0·2325	*w*	343
402	—	0·2498	—	< 1
303	—	0·2573	—	147
031	—	0·2729	—	22
004	—	0·2768	—	151
412	—	0·2782	—	< 1
123	—	0·2806	—	< 1
131	0·2841	0·2842	*vw*	96
322		0·2844		215

s = strong, *m* = medium, *w* = weak, *vw* = very weak.

The powder photographs of samples whose composition was close to 50 at.% palladium could be indexed on the basis of an orthorhombic lattice with $a = 7{\cdot}249 \pm 0{\cdot}005$, $b = 4{\cdot}571 \pm 0{\cdot}003$, $c = 5{\cdot}856 \pm 0{\cdot}004$ Å, and observed and calculated values of $\sin^2\theta$ are given in Table 1. The systematic extinctions and lattice parameters suggested that ThPd might be isostructural with ThSi (Jacobson, Freeman, Tharp & Searcy, 1956) with the FeB structure (*B*27), space group *Pnma* (D_{2h}^{16}). This structure requires four formula units per unit cell giving a calculated density of 11·60 g.cm^{-3}. The density was not measured experimentally.

The atomic positions for this structure are:

$$4\,\mathrm{Th}\ \text{in}\ \ \pm(x_{\mathrm{Th}}, \tfrac{1}{4}, z_{\mathrm{Th}}) \pm (\tfrac{1}{2} + x_{\mathrm{Th}}, \tfrac{1}{4}, \tfrac{1}{2} - z_{\mathrm{Th}})$$
$$4\,\mathrm{Pd}\ \text{in}\ \ \pm(x_{\mathrm{Pd}}, \tfrac{1}{4}, z_{\mathrm{Pd}}) \pm (\tfrac{1}{2} + x_{\mathrm{Pd}}, \tfrac{1}{4}, \tfrac{1}{2} - z_{\mathrm{Pd}})$$

and trial atomic parameters, based on those of ThSi, of $x_{\mathrm{Th}} = 0{\cdot}18$, $z_{\mathrm{Th}} = 0{\cdot}125$, $x_{\mathrm{Pd}} = 0{\cdot}03$, $z_{\mathrm{Pd}} = 0{\cdot}61$ gave a fairly good fit to the observed intensities. These atomic parameters were refined with the A.E.R.E. Ferranti 'Mercury' computer and structure factors were computed for a series of trial structures. Atomic parameters of

$$x_{\mathrm{Th}} = 0{\cdot}180 \pm 0{\cdot}002, \quad z_{\mathrm{Th}} = 0{\cdot}124 \pm 0{\cdot}002,$$
$$x_{\mathrm{Pd}} = 0{\cdot}030 \pm 0{\cdot}0025, \quad z_{\mathrm{Pd}} = 0{\cdot}630 \pm 0{\cdot}0025$$

gave the best agreement between observed and calculated intensities which are shown in Table 1. Isotypes of ThPd therefore include ThSi, ZrSi, FeB (Pearson, 1958) and GdPt (Baenziger & Moriarty, 1961).

With the above atomic positions the following interatomic distances were obtained:

Th–1 Pd	2·94 Å	Pd–2 Pd	2·78 Å
1 Pd	3·09	1 Th	2·94
4 Pd	3·10	1 Th	3·09
1 Pd	3·16	4 Th	3·10
2 Th	3·76	1 Th	3·16
4 Th	3·85		
2 Th	3·91		
2 Th	4·57		

The total coordination around the thorium and palladium atoms of 17 and 9 respectively is the same as that around the thorium and X atoms in the six ThX compounds of the CrB type (Thomson, 1962) although the detailed arrangements differ in the two structures. In both, the non-thorium atoms form zigzag chains through the lattice and the shortest Th–X distances show a decrease of about 7% compared with those obtained by addition of Pauling's values for the atomic radii for C.N. 12 (Pauling, 1956). The decreased Th–X distances suggest that there might be appreciable Th–X interaction in both types of compound. In a recent discussion of the interatomic distances in several other compounds formed between thorium and palladium (Thomson, 1963*b*) it was pointed out that the closest Th–Pd distance tends to increase with increasing thorium composition and this trend is continued in ThPd.

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* Formerly J. R. Murray.

Aronsson (1961) noted that the occurrence of the FeB structure usually depends on a favourable radius ratio $r_X/r_M \simeq 0.7$ and the ratio $r_{Pd}/r_{Th} = 0.77$ is in general agreement with this observation. It is of interest to note that in several systems where compounds of the FeB type occur, compounds of the $CuAl_2$ (*C*16) type have also been observed, *e.g.* Hf–Si, Zr–Si, Mn–B, Co–B and Th–Pd.

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References

Aronsson, B. (1960). *Ark. Kemi*, **16**, 379.
Baenziger, N. C. & Moriarty, J. L. (1961). *Acta Cryst.* **14**, 946.
Jacobson, E. L., Freeman, R. D., Tharp, A. G. & Searcy, A. W. (1956). *J. Amer. Chem. Soc.* **78**, 4850.
Pauling, L. (1956). *Theory of Alloy Phases*, p. 232. Amer. Soc. Met.
Pearson, W. B. (1958). *Handbook of Lattice Spacings and Structures of Metals.* London: Pergamon Press.
Thomson, J. R. (1962). *Acta Cryst.* **15**, 1308.
Thomson, J. R. (1963*a*). *J. Less-Common Metals.* In the press.
Thomson, J. R. (1963*b*). *Acta Cryst.* **16**, 320.

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The structure of $SrZn_2$.

By B. G. Bergman* and P. J. Shlichta†, *Gates and Crellin Laboratories of Chemistry‡, California Institute of Technology, Pasadena, California, U.S.A.*

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An investigation of the strontium–zinc system (Bergman & Shlichta, to be published) disclosed a phase, in slowly cooled alloys of 40 to 60% wt. zinc, characterized by prismatic crystals embedded in a eutectic matrix. Both crystals and matrix had to be stored under hexane to prevent reaction with air.

A chemical analysis of 50 mg of crystals, selected from an alloy containing 40% wt. zinc, indicated a composition of 55·6% wt. zinc. An alloy of 55% wt. zinc gave an X-ray powder pattern almost identical with that of the pulverized crystals; the density of this sample was 4·71 g.cm^{-3}.

Laue photographs from a single crystal, 0·2 mm long, indicated orthorhombic symmetry. The unit-cell edges, as determined by rotation and Weissenberg photographs, were $a = 4{\cdot}78$ Å, and $b \simeq c = 7{\cdot}80$ Å. The refined values, obtained from extreme high-angle reflections recorded on films asymmetrically mounted in a precision rotation camera, were

$$a = 4{\cdot}779 \pm 0{\cdot}002, \quad b = 7{\cdot}795 \pm 0{\cdot}001, \quad c = 7{\cdot}820 \pm 0{\cdot}001 \text{ Å};$$

the precision was estimated from the differences between the Cu $K\alpha_1$ ($\lambda = 1{\cdot}5405$ Å) and Cu $K\alpha_2$ ($\lambda = 1{\cdot}5443$ Å) reflections. All of the 180 Weissenberg reflections observed on the layers $h = 0$, 1, 2, 3, and 4 were of the kind $h + k + l = 2n$ and $h = 2n$, $k = 2n$, $l = 0$. These indicated a body-centered unit cell with a glide plane perpendicular to the c axis. Hence, the probable space groups were *Imma* (D_{2h}^{28}) and *Im*2*a* (C_{2v}^{22}) both having a minimum multiplicity of four.

The measured density, chemical analysis, and unit-cell volume correspond to a unit cell content of $Sr_{4{\cdot}14}Zn_{7{\cdot}00}$, but, because of the fourfold multiplicity, the only permissible unit cell content for an ordered structure is Sr_4Zn_8; *i.e.* 59·8% wt. zinc with $\varrho = 4{\cdot}98$ g.cm^{-3}.

Layer lines with alternate values of h had closely similar intensity distributions, indicating that the structure consisted of planar layers, perpendicular to the a axis, with a spacing of $a/2$. The only permissible positions for the four strontium atoms, compatible with their large size and the layering and symmetry requirements, are 4(e) of *Imma* (D_{2h}^{28}), namely $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) + 0, \frac{1}{4}, z;\ 0, \frac{3}{4}, \bar{z}$, where $z < 0{\cdot}10$. This arrangement leaves holes appropriate for the accommodation of eight zinc atoms at 8(h): $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) + 0, y, z;\ 0, \bar{y}, \bar{z};\ 0, (\frac{1}{2} + y), \bar{z};\ 0, (\frac{1}{2} - y), z$, where $y > 0{\cdot}90$ and $z \simeq 0{\cdot}33$. Equalization of the Sr–Sr and of the Zn–Zn contact distances yields $z = 0{\cdot}051$ for Sr and $y = 0{\cdot}95$, $z = 0{\cdot}325$ for Zn. Trial and error adjustment, to obtain the best qualitative agreement with the $0k0$ and $00l$ reflections, resulted in $z = 0{\cdot}049$ for Sr and $y = 0{\cdot}941$, $z = 0{\cdot}338$ for Zn. The intensities calculated from these parameters gave good

Table 1. *Refinement of parameters*

		Trial and error	Least squares 1st	Least squares 2nd
4 Sr in 4(e)	x	0	0	0
	y	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
	z	0·049	0·051	0·052
8 Zn in 8(h)	x	0	0	0
	y	0·941	0·939	0·939
	z	0·338	0·335	0·335
	B_y	0·238	1·086	0·006
	B_z			1·019
	R	23·1%	17·9%	17·6%

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* Present address: National Engineering Science Company, Pasadena, California.

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