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Crystal Structure of the New Thorium Intermetallics ThIn and Th_6Cd_7

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The title phases are orthorhombic: ThIn, *oP*24, space group *Pbcm*, $a = 10.806(3)$ Å, $b = 9.954(4)$ Å, $c = 6.520(4)$ Å, $Z = 12$; Th_6Cd_7, *oP*26, space group *Pbam*, $a = 11.703(3)$, Å, $b = 9.929(7)$ Å, $c = 6.041(2)$ Å, $Z = 2$. Direct methods were used for both structure solutions on data collected with an automated single crystal X-ray diffractometer. Anisotropic refinements gave $R = 0.065$ for ThIn and $R = 0.086$ for Th_6Cd_7 using 799 and 1015 reflections, respectively. The structure of ThIn is closely related to the hexagonal Ti_5Ga_4 type, from which it can be geometrically derived. Th_6Cd_7 can be regarded as a tetrahedrally close packed structure where the Th atoms present the typical CN 14, CN 15, and CN 16 Frank–Kasper polyhedra and the Cd atoms are icosahedrally coordinated.

Introduction

For several years we have studied the thermodynamic and crystallographic data of binary intermetallic compounds of thorium. The aim of this work is to provide a complete crystallochemical data set in order to compare thorium with the rare earth and alkaline earth metals so that the influence of the change in valence electron concentration, in passing from tetra- to tri- and divalent elements, on the existence, stability, and structure of the intermediate phases may be studied.

The lack of information concerning the Th–Cd and Th–In systems (*1*) led us to completely redetermine these two phase diagrams. In the Th–Cd system six intermediate compounds were found, five of which were identified, while a "ThCd" phase, close to the equiatomic composition, showed an unknown structure (*2*). A similar situation has also been found in the Th–In system where the structure of ThIn, one of the four present phases, remained unresolved (*3*). In this paper we report the results of the crystal structure determination of these two new phases, Th_6Cd_7 and ThIn.

Experimental and Structure Determination

No particular difficulties were encountered in the preparation of the samples. Fine turnings of the pure elements (Th 99.5%, Cd and In 99.99% from Koch-Light, England) were well mixed, pressed together, closed in molybdenum crucibles, and allowed to react at high temperature (about 1673 K for ThIn and 1373 K for Th_6Cd_7) following the indications of the phase diagrams. The alloys were annealed for a short time a few degrees below the decomposition or the melting point. To improve

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the formation of single crystals for structural determination the samples were prepared at a composition a little different from the stoichiometric one: 52.5 at.% Th for ThIn and 48.5 at.% Th for Th_6Cd_7.

Special care must be taken because of the very high reactivity of these alloys with moist air. As found in many other systems of thorium the reactivity is highest around the equiatomic composition: the samples decompose very rapidly and are often pyrophoric.

To avoid oxidization during the examination of the crystals, small fragments of each were put in vaseline oil, previously dried over metallic sodium and evacuated 24 hr at 373 K. Single crystals of the two compounds, sealed in glass capillaries under vacuum, were mounted on an Enraf–Nonius CAD-4 automatic diffractometer. The lattice constants were determined by least-squares refinement of 25 high-angle reflections measured using graphite-monochromated Mo$K\alpha$ radiation (λ = 0.71069 Å).

The crystal of ThIn (0.03 × 0.05 × 0.19 mm) have orthorhombic symmetry with a = 10.806(3) Å, b = 9.954(4) Å, c = 6.520(4) Å, and extinctions ($0kl$, $k \neq 2n$; $h0l$, $l \neq 2n$) consistent with the space groups $Pca2_1$ and $Pbcm$.

The crystal of Th_6Cd_7 (0.07 × 0.18 × 0.30 mm) also have orthorhombic symmetry with a = 11.703(3) Å, b = 9.929(7) Å, c = 6.041(2) Å, and extinctions ($0kl$, $k \neq 2n$; $h0l$, $h \neq 2n$) consistent with the space groups $Pba2$ and $Pbam$.

For both crystals intensities of two octants were collected in the $\omega - \vartheta$ scan mode up to $2\vartheta = 60°$. Owing to the strong absorption effect (μ = 103 mm^{-1} for ThIn and 102 mm^{-1} for Th_6Cd_7) and the irregular shape of the crystals, both the spherical correction and the semi-empirical correction based on the azimuthal scan data of several top reflections (*4*) were applied. The independent reflections were 1104 for ThIn and 1115 for Th_6Cd_7.

Each structure was solved in the corresponding centrosymmetric space group by direct methods with SHELX 76 (*5*) and refined by full-matrix least squares based on F's using reflections with $F_o > 3\sigma(F_o)$ and weight $w = 1/\sigma^2(F_o)$. The atomic scattering factors and corrections for anomalous dis-

TABLE I

ATOMIC COORDINATES, ISOTROPIC EQUIVALENT, AND ANISOTROPIC (× 10^3) THERMAL PARAMETERS

	x	y	z	U_{eq} (Å^2)	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
ThIn (*Pbcm*)										
Th(1) in 4(*d*)	0.8810(2)	0.4680(3)	0.25	0.015(1)	10(1)	19(1)	16(1)	0	0	0(1)
Th(2) in 4(*d*)	0.3097(2)	0.3703(3)	0.25	0.016(1)	11(1)	22(1)	17(1)	0	0	1(1)
Th(3) in 4(*c*)	0.6143(2)	0.25	0	0.021(1)	11(1)	35(2)	16(1)	0(1)	0	0
In(1) in 4(*d*)	0.8585(4)	0.1330(5)	0.25	0.018(2)	11(2)	21(2)	23(2)	0	0	−1(2)
In(2) in 4(*d*)	0.4158(5)	0.0450(6)	0.25	0.030(3)	15(2)	26(3)	49(4)	0	0	0(2)
In(3) in 4(*c*)	0.0698(4)	0.25	0	0.018(2)	12(2)	21(2)	21(2)	1(2)	0	0
Th_6Cd_7 (*Pbam*)										
Th(1) in 4(*h*)	0.0835(2)	0.1622(3)	0.5	0.030(1)	36(1)	12(1)	41(1)	0	0	1(1)
Th(2) in 4(*h*)	0.1297(2)	0.5477(3)	0.5	0.028(1)	36(1)	10(1)	37(1)	0	0	−1(1)
Th(3) in 4(*g*)	0.0453(2)	0.3413(3)	0	0.027(1)	36(1)	8(1)	36(1)	0	0	0(1)
Cd(1) in 8(*i*)	0.1830(4)	0.8416(5)	0.2566(8)	0.034(2)	45(2)	13(2)	44(2)	0(2)	1(2)	−3(2)
Cd(2) in 4(*g*)	0.2510(6)	0.0942(7)	0	0.035(2)	47(3)	9(2)	48(3)	0	0	2(2)
Cd(3) in 2(*a*)	0	0	0	0.019(3)	25(3)	1(3)	30(3)	0	0	1(2)

Notes. The thermal factors are expressed as $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^*)]$. $U_{eq} = (1/3)(U_{11} + U_{22} + U_{33})$. The esd's are given in parentheses.

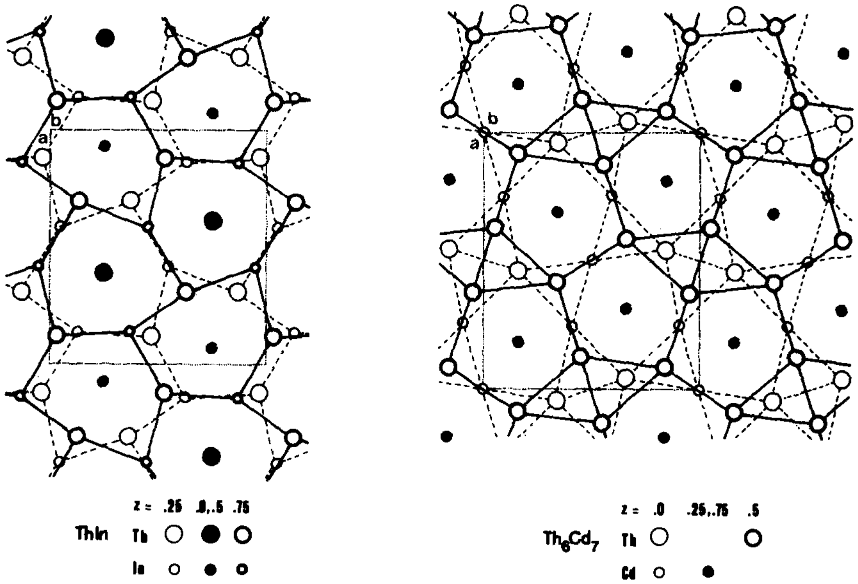

FIG. 1. Projection of the structures of ThIn and Th_6Cd_7 along the *c* axis.

persion were taken from *International Tables for X-Ray Crystallography* (*6*). The final anisotropic refinement converged at $R = 0.065$ for ThIn (799 reflections, 35 parameters) and $R = 0.086$ for Th_6Cd_7 (1015 reflections, 38 parameters).

Table I lists the positional and thermal parameters of the two compounds.[1]

Discussion

The structures of ThIn and Th_6Cd_7, which represent new types, are characterized by the alternation along the short *c* axis (~6 Å) of densely and scarcely populated layers of atoms, *c*/4 apart. Projection of the two structures along this axis is shown in Fig. 1.

In ThIn all layers have 1 : 1 composition. Nets formed by two kinds of very distorted hexagons are found at $z = \frac{1}{4}$ and $z = \frac{3}{4}$ and their nearly antisymmetric stacking generates two kinds of polyhedra centered by Th(3) and In(3). These atoms form nets with Schläfli symbol 3^6 at $z = 0$ and $z = \frac{1}{2}$.

TABLE II

INTERATOMIC DISTANCES IN ThIn UP TO 3.8 Å FOR In–In AND UP TO 4.4 Å FOR ALL OTHER DISTANCES[a]

Th(1)– In(1)	3.26	Th(2)– In(1)	3.18
–2In(3)	3.29	–2In(3)	3.29
– In(2)	3.30	– In(2)	3.44
– In(1)	3.34	– In(2)	3.44
–2In(3)	3.40	–2In(2)	3.56
–2In(1)	3.42	–2Th(3)	3.86
–2Th(3)	3.96	–2Th(2)	4.05
–2Th(2)	4.18	–2Th(1)	4.18
–2Th(1)	4.20	–2Th(3)	4.20
Th(3)–2Th(3)	3.26	In(1)–2In(3)	3.04
–2In(1)	3.31	– Th(2)	3.18
–2In(2)	3.37	– Th(1)	3.26
–2In(2)	3.38	–2Th(3)	3.31
–2Th(2)	3.86	– Th(1)	3.34
–2Th(1)	3.96	–2Th(1)	3.42
–2Th(2)	4.20		
In(2)– Th(1)	3.30	In(3)–2In(1)	3.04
–2Th(3)	3.37	–2In(3)	3.26
–2Th(3)	3.38	–2Th(2)	3.29
– Th(2)	3.44	–2Th(1)	3.29
– Th(2)	3.44	–2Th(1)	3.40
–2Th(2)	3.56		

[a] esd's are less than 0.01 Å.

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[1] Lists of observed and calculated structure factors can be obtained from the authors on request.

In Th_6Cd_7 two pentagon–triangle main layers, containing either Th and Cd atoms or Th only, are stacked in such a way that pentagons of one layer cover those of the other antisymmetrically, and are interleaved by Cd secondary nets with Schläfli symbol 3^2434.

Inspection of the interatomic distances reported in Table II and Table III gives another point of similarity: in both structures short Th–Th distances are present, 3.26 Å in ThIn and 3.18 Å in Th_6Cd_7, 9 and 12%, respectively, smaller than the metallic diameter of Th after Teatum *et al.* (*7*). Analogous short Th–Th distances were found in other phases of the Th–Sn (*8*) and Th–Pb (*9*) systems, namely, in Th_5Sn_3 and Th_5Pb_3 with the Mn_5Si_3 structure (3.24 and 3.26 Å, respectively) and in Th_5Sn_4 and Th_5Pb_4 with a filled-up Mn_5Si_3 structure, Ti_5Ga_4 type (3.22 and 3.29 Å, respectively).

TABLE III

INTERATOMIC DISTANCES IN Th_6Cd_7 UP TO 4.9 Å[a]

Th(1)-2Cd(1)	3.45	Th(2)- Th(2)	3.18
-2Th(3)	3.53	-2Cd(1)	3.33
- Th(2)	3.54	-2Cd(1)	3.34
-2Cd(3)	3.56	-2Cd(2)	3.36
-2Cd(1)	3.58	- Th(1)	3.54
-2Cd(2)	3.66	-2Th(3)	3.78
-2Cd(1)	3.69	- Th(1)	3.81
- Th(1)	3.77	-2Th(3)	3.81
- Th(2)	3.81	- Th(1)	3.87
- Th(2)	3.87		
		Cd(1)- Cd(1)	2.94
Th(3)- Th(3)	3.33	- Cd(2)	3.01
- Cd(3)	3.43	- Cd(2)	3.05
- Cd(2)	3.44	- Cd(3)	3.08
- Cd(2)	3.46	- Cd(1)	3.10
- Cd(2)	3.50	- Th(2)	3.33
-2Th(1)	3.53	- Th(2)	3.34
-2Cd(1)	3.54	- Th(1)	3.45
-2Cd(1)	3.58	- Th(3)	3.54
-2Th(2)	3.78	- Th(1)	3.58
-2Th(2)	3.81	- Th(3)	3.58
		- Th(1)	3.69
Cd(2)-2Cd(1)	3.01		
-2Cd(1)	3.05	Cd(3)-4Cd(1)	3.08
- Cd(3)	3.08	-2Cd(2)	3.08
-2Th(2)	3.36	-2Th(3)	3.43
- Th(3)	3.44	-4Th(1)	3.56
- Th(3)	3.46		
- Th(3)	3.50		
-2Th(1)	3.66		

[a] esd's are less than 0.01 Å.

The atomic arrangements of ThIn and Th_5Sn_4 show a close relationship. In Table IV the distances in Th_5Sn_4 are given for a comparison. The coordination polyhedra around Th(2), Th(3), and In(2) in ThIn are identical to those around Th(2), Th(1), and Sn(2) in Th_5Sn_4, respectively, with In(2) and Sn(2) presenting the same tricapped trigonal prism formed by nine thorium atoms. Moreover, the polyhedron of Th(1) in ThIn is very similar to that of Th(2) in Th_5Sn_4, but with a pair of Th replaced by two In atoms, and In(3) resembles somewhat Sn(1), having six Th arranged as a distorted octahedron, capped by two In atoms, but with a face enlarged to allow contact with two other In. On the other hand, the coordination around In(1) is completely different. It is surrounded by a very distorted Th pentagonal bipyramid with insertion of two further In atoms.

The similarity between the two structures of ThIn and Th_5Sn_4 can be seen in Fig. 2, where the polyhedra of Th(1) and Th(2)

TABLE IV

INTERATOMIC DISTANCES IN Th_5Sn_4 (Ti_5Ga_4 TYPE) UP TO 3.9 Å FOR Sn–Sn AND UP TO 4.5 Å FOR ALL OTHER DISTANCES[a]

$P6_3/mcm$, $a = 9.643$ Å, $c = 6.445$ Å
Th(1) in 4(*d*); Th(2) in 6(*g*) with $x = 0.2800(4)$;
Sn(1) in 2(*b*); Sn(2) in 6(*g*) with $x = 0.6186(8)$.

Th(1)-2Th(1)	3.22	Sn(1)-6Th(2)	3.14
-6Sn(2)	3.41	-2Sn(1)	3.22
-6Th(2)	3.85		
		Sn(2)- Th(2)	3.27
Th(2)-2Sn(1)	3.14	-2Th(2)	3.30
- Sn(2)	3.27	-2Th(2)	3.37
-2Sn(2)	3.30	-4Th(1)	3.41
-2Sn(2)	3.37		
-4Th(1)	3.85		
-4Th(2)	4.20		

[a] esd's are less than 0.01 Å.

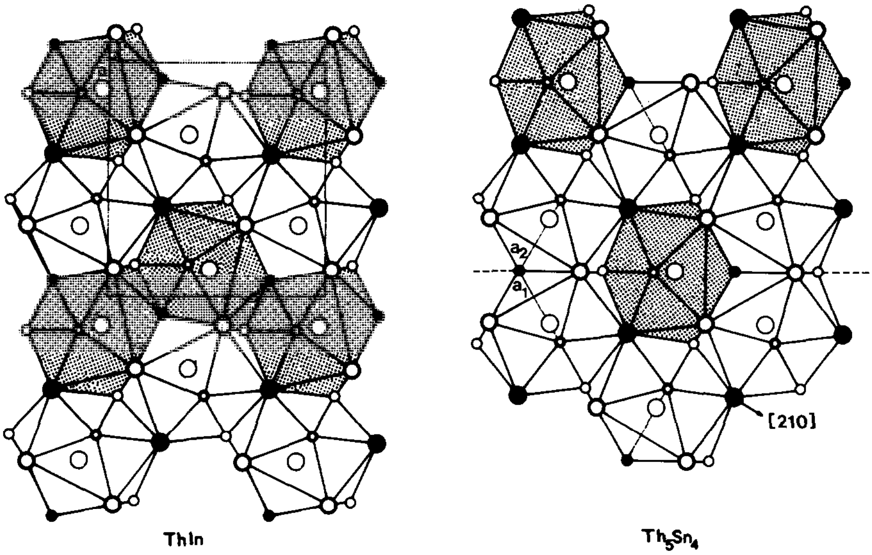

FIG. 2. Coordination polyhedra around Th(1) (stippled) and Th(2) in ThIn, and around Th(2) in Th_5Sn_4.

in ThIn and Th(2) in Th_5Sn_4 are drawn. To facilitate the comparison, the Th(1) polyhedra of ThIn and some of the Th(2) polyhedra of Th_5Sn_4 are stippled. A possible mechanism to obtain the structure of ThIn can be devised by cutting the cell of the hexagonal Th_5Sn_4 along the dashed line, shifting the lower half cell of the quantity $a\sqrt{3}/3$ in the [210] direction and replacing a pair of Th with two In atoms in the upper stippled polyhedra. These operations destroy the hexagonal symmetry and lead to a different stoichiometry.

The structure of the phase Th_6Cd_7 can be classified as a tetrahedrally close packed Frank–Kasper structure. It is well known that this family is characterized by the presence of interpenetrating coordination polyhedra with 12 (icosahedron), 14, 15, or 16 vertices and triangular faces, which originate a distorted tetrahedral packing of atoms with good space filling. Indeed, Th(1), Th(2), and Th(3) show the CN 16, CN 14, and CN 15 Frank–Kasper polyhedron, respectively, whereas Cd(1), Cd(2), and Cd(3) are icosahedrally surrounded (CN 12).

It is interesting to note that a structure with this composition was first foreseen by the same Frank and Kasper (*10*) and later by Shoemaker and Shoemaker (*11*), and by Kripyakevich (*12*). In particular, Kripyakevich classified this hypothetic structure in the homologous series obtained by combining fragments of the Zr_4Al_3 type and the Laves phase $MgZn_2$, and also predicted the correct space group.

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