COMPOUNDS OF THORIUM WITH TRANSITION METALS

I. The Thorium-Manganese System

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COMPOUNDS OF THORIUM WITH TRANSITION METALS

I. THE THORIUM-MANGANESE SYSTEM[*]

by

John V. Florio, R. E. Rundle and A. I. Snow[**]

Abstract

Like uranium, thorium forms no compounds with chromium, a few with manganese, the number increasing through nickel, and decreasing sharply with copper. The structures of the compounds of thorium with manganese, reported in detail here, are unlike those with iron, cobalt and nickel, which are generally similar.

$ThMn_2$ has the $MgZn_2$ (Cl4-type) structure, Th_6Mn_{23} is face-centered cubic with a unique structure, while $ThMn_{12}$ is body-centered tetragonal with a structure similar to, but not identical with the corresponding iron, cobalt and nickel compounds.

Introduction

The compounds of thorium with the transition elements of the first period are particularly numerous and interesting, and display several new structural types. The present empirical stage in the development of theories of intermetallic compound formation

suggests that further structural studies will be important aids to progress in this field. We have, therefore, undertaken a systematic study of the structures of intermetallic compounds of thorium with the transition metals.

Like uranium (Baenziger, et al. 1950), thorium forms no compounds with chromium, a few with manganese, the number increasing through nickel, and falling abruptly with copper. Other than this, there is little similarity in the compounds of thorium and uranium with transition metals. Structure of the manganese compounds, given in detail here, differ from those of iron, cobalt and nickel compounds, which are very similar. The latter will be reported together in a subsequent paper, but a summary of the known compounds, stable at room temperature, is given in Table I.

Determination of Phases

The study of the Th-Mn system was first made by means of X-ray powder data in order to determine the number and approximate composition of the phases stable at room temperature. No attempt has been made to find phases stable at any other temperature.

Due to the high volatility of manganese it was difficult to obtain homogeneous samples, especially at high manganese concentrations. To help overcome this difficulty the samples were prepared under an inert atmosphere. Alloys with compositions ranging from 12 to 96 atomic per cent manganese were examined. All the samples were analyzed chemically within an accuracy of 1% or better.

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Table I

Compounds of Thorium with First Period Transition Metals

Cr	Mn	Fe	Co	Ni	Cu
		Th_7Fe_3 [a,b]	Th_7Co_3 [a,b]	Th_7Ni_3 [a,b]	
					$Th_2Cu(CuAl_2)$
(None)		$ThFe$ [b,c]	$ThCo$ [b]	$ThNi$ [b]	
	$ThMn_2(C14)$ [d]	$ThFe_{2-3}$ [b,c]	$ThCo_{2-3}$ [b,c]	$ThNi_2(AlB_2)$	$ThCu_2(AlB_2)$
	Th_6Mn_{23} [b]				
		$ThFe_5(CaZn_5)$ [e]	$ThCo_5(CaZn_5)$	$ThNi_5(CaZn_5)$	
	$ThMn_{12}$ [b]	$ThFe_{12}$ [b,f]	$ThCo_{12}$ [b,f]	$ThNi_{12}$ [b,f]	

[a] N. C. Baenziger, Thesis, Iowa State College (1948).

[b] New structural type.

[c] Structure not yet fully known.

[d] Strukturbericht designation.

[e] Existence suspected from limited data which suggest it is isomorphous with corresponding Ni compound.

[f] Not identical with manganese compound, structural work not complete.

Aside from the oxide, ThO_2, the carbide, ThC, and the elements themselves, the powder diagrams indicated the presence of three other phases with compositions of roughly 67, 80, and 92 atomic per cent manganese. Single crystals of the three compounds existing in these regions were obtained. It was then possible to index all the powder lines due to these phases.

There were not enough single crystals to perform a direct chemical analysis or to run a density determination using a pycnometer on material known to be strictly a single phase. The crystals were too dense to permit ordinary flotation methods for density determinations. The formulas representing the compounds $ThMn_2$, Th_6Mn_{23}, and $ThMn_{12}$ are based upon the rough chemical composition, atomic volume and space group considerations, and, finally, upon complete structure determinations.

ThMn₂

Powder data and single crystal data taken with a Buerger precession camera, Mo Kα radiation ($\lambda = 0.7107$ Å), $\mu = 30°$, and a magnification factor of 5.5 were obtained. The latter data included precession about the hexagonal axis, $\underline{/10 \cdot 0 \underline{/}}$ and $\underline{/21 \cdot 0 \underline{/}}$. Both powder and precession diagrams require a hexagonal lattice, $a_0 = 5.48 \pm 0.01$ Å, $c_0 = 8.95 \pm 0.02$ Å. Precession diagrams about c_0 exhibited C6ℓ symmetry in all levels, while the $\underline{/10 \cdot 0 \underline{/}}$ and $\underline{/21 \cdot 0 \underline{/}}$ diagrams possessed C2ℓ symmetry in all levels. Reflections (HH·L) were absent for L odd, so the space group is D_{6h}^4 - C6/mmc or C_{6v}^4 - C6mc.

This phase, occurring at approximately 67 atomic % manganese, had an axial ratio and symmetry suggesting that it was isomorphous with $MgZn_2$ (C-14 structure type). Structure factors calculated for the ideal structure,

$4Th$ at $\pm$ $(\frac{1}{3},\frac{2}{3},z)$; $\pm$ $(\frac{2}{3},\frac{1}{3},\frac{1}{2}$ + $z)$; $z = 1/16$

$2Mn$ at 000; $00\frac{1}{2}$

$6Mn$ at $\pm$ $(x,\ 2x,\ \frac{1}{4})$; $\pm$ $(2\ \bar{x},\ \bar{x},\ \frac{1}{4})$; $\pm$ $(x,\ \bar{x},\ \frac{1}{4})$; $x = -\frac{1}{6}$,

were compared with structure factors obtained from timed exposures using the precession camera. The calculated and observed structure factors are given in Table II. The correlation factor, R =

$$\sum \left| |F_{obsd.}| - |F_{calcd.}| \right| / \sum |F_{obsd.}|$$ was 0.13 for (HK·L) data.

A trial and error attempt was made to refine the z_{Th} parameter. The ideal value appears, however, to be excellent. For example, from a set of timed exposures yielding (HH·L) data it was found that

$F_{(11\cdot6)} > 4.4\ F_{(11\cdot4)}, F_{(22\cdot2)} > 4.4\ F_{(11\cdot4)},\ F_{(11\cdot6)} \approx F_{(22\cdot2)}$

and $F_{(22\cdot2)} > 1.4\ F_{(11\cdot6)}$. These reflections occur at nearly the same $\sin\theta$, and should have very similar temperature and adsorption corrections in the technique employed. From these it can be shown that $z_{Th} = 0.0625 \pm 0.002$. A Fourier projection on to (00·1) led to a manganese parameter of 0.167, ideal within our observation.

From interatomic distances in Table III and Pauling's rules and radii (1947), the metallic valences of thorium and manganese in the compound, i.e., the number of electrons used in bonding, are calculated to be 6.28 for thorium and 2.58 for manganese. These

Table II

Calculated and Observed Structure Factors for $ThMn_2$

	$F_{calcd.}$	$F_{obsd.}$
(100)	− 97	106
(200)	− 162	180
(300)	+ 252	231
(400)	− 121	150
(500)	− 68	40
(600)	+ 159	183
(110)	+ 296	322
(120)	− 85	90
(130)	− 78	70
(140)	+ 204	193
(150)	− 65	41
(220)	+ 338	336
(230)	− 72	57
(240)	− 106	80
(250)	+ 174	142
(330)	+ 184	197
(340)	− 62	50
(002)	+ 144	104
(004)	+ 142	138
(006)	− 229	190
(008)	− 122	107
(0010)	− 173	207
(112)	+ 274	282
(114)	0	0
(116)	− 112	100
(118)	− 204	214
(1110)	− 93	117
(222)	+ 112	100
(224)	+ 91	105
(226)	− 185	187
(228)	− 112	171
(332)	+ 174	163

are in poor agreement with the expected value of 4 for thorium and those of 4.16 and 5.78 given by Pauling for manganese.

Table III

Interatomic Distances in $ThMn_2$

Th		4 Th	3.35 Å
		12 Mn	3.21 Å
Mn_I (000), etc.		6 Th	3.21 Å
		6 Mn	2.74 Å
Mn_{II} (1/3 1/6 1/4), etc.		6 Th	3.21 Å
		6 Mn	2.74 Å

Th_6Mn_{23}

Unit Cell and Space Group.- An alloy with 81.8 atomic % manganese was essentially a single phase. Single crystals were found in this alloy, and proved to be cubic with Laue symmetry O_h, as determined by precession diagrams. The lattice constant was a_0 = 12.523 ± 0.001 Å as determined using a cylindrical back reflection powder camera of 5.0 cm. radius and the method of Jette and Foote (1935).

The multiple film technique of Robertson (1943) was used to obtain rotation and zero-level Weissenberg diagrams for rotation about a four-fold axis. Cu Kα radiation (λ = 1.5418 Å) and a camera of 5.73 cm. were employed.

Absences characteristic of a face-centered lattice were the only ones noted. The space group is, therefore, T_d^2 - $F\overline{4}3m$, O^3-F43 or O_h^5 - $Fm3m$.

Composition of the Phase.- From the powder data, the approximate composition of the phase appeared to be $ThMn_4$. The density of the essentially one phase alloy at 81.8 atomic % manganese was 9.02 ± 0.05 g/cc. From the lattice constant there would then be 23.6 $ThMn_4$ per unit cell. Since the cell is face-centered, the number of thorium and manganese per unit cell must each be divisible by four. Consequently, the density and approximate composition are good enough to establish the number of thorium atoms per unit cell as 24. The experimental density, however, is roughly satisfied by either 88, 92, 96 manganese per unit cell. Assuming Mehl's modification of Vegard's law (1928) to apply, and taking the atomic volume of thorium as 32.8 $\overset{o}{A}^3$ and that of manganese as 12.4 $\overset{o}{A}^3$, the volume of the unit cell suggests that there are 94 manganese atoms per unit cell, in satisfactory agreement with 92 or 96. The composition was tentatively assumed to be $ThMn_4$ (96 Mn per unit cell), and the final decision on the composition had to await a complete structure determination.

Atomic Positions.- In the three possible space groups there are three unique twenty-four fold positions; 24 (d) and (e) of space groups $Fm3m$ and F43, and 24 (g) of $F\overline{4}3m$. In addition, 24 (f) of $F\overline{4}3m$ is equivalent to 24 (e).* The twenty-four thoriums are

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*Positions are given the designation found in "International Tables for the Determination of Crystal Structures" (1935).

almost certainly in one of these sets, since combinations of four, eight and sixteen-fold sets include a number of parameter-less sets, and are easily eliminated. The parameterless set, 24 (d), is incompatible with the X-ray data, while the stronger peaks on the Patterson, P(xy), Fig. 1, can be interpreted in terms of the one-parameter sets, either 24 (e) or 24 (g), with x = 12/60 or 3/60 respectively. On the Patterson section, P(xy0), 24 (e) requires peaks on the diagonal at (xxo), while 24 (g) requires off diagonal peaks. The important peaks on this Patterson section are on diagonals and are compatible only with the set, 24 (e), with x = 12/60. The subsequent structure determination substantiates this choice.

To find manganese positions we again consider the Patterson projection, P(xy), Fig. 1. The 96-fold sets from the three possible space groups all require important Th-Mn peaks off the diagonals, whereas all important Patterson peaks are found on the diagonals. Consequently, all 96-fold sets are eliminated. The 48-fold set involving two parameters, 48 (h) of $F\bar{4}3m$, is eliminated for a similar reason unless z = 0 or $\frac{1}{2}$, when it becomes essentially identical with 48 (h) or 48 (i) of Fm3m, or cor- responding positions in F43. These 48-fold sets are eliminated by consideration of the two-dimensional Patterson, P (xy), to- gether with the Patterson section, P (xy 12/60), since important Th-Mn peaks on the projection should appear again on the section corresponding to the thorium parameter. None of the expected peaks appear on P (xy 12/60). The only other 48-fold sets;

48 (g) of Fm3m or 48 (i) of F43, require Th-Mn peaks on P (xy) at $(\frac{1}{4},\frac{1}{4})$, $(\frac{1}{4},x)$ and $(\frac{1}{4}, 3/60)$. Though some indication of peaks, with x = 8/60 are found, these are so far from the expected magnitudes that this possibility seemed unpromising.

Turning to 32-fold sets, it was found that by placing 64 manganese atoms in 32 (f) of Fm3m or F43, with x_1 = 11/60, x_2 = 23/60, and in addition, placing manganese in 24 (d) and 4 (b), both parameterless sets, the two dimension Patterson, Fig. 1, is accounted for except for what we believe to be a diffraction ring around the origin, and a very small peak at $(\frac{1}{4}, 8/60)$. These positions are all found in Fm3m and F43, and are permitted in F43m if the 32 fold sets are split into two 16-fold groups, with x_a = $\bar{x}_b$. Consequently, we may take the space group as Fm3m.

We have checked this structure by calculating the three dimensional Patterson function for the levels z = 0, 3/60, 7/60, 12/60, 14/60 and 15/60, which should contain all the important Th-Th and Th-Mn terms. In all cases, agreement with expectations based on the above structure was good, and a preliminary check of observed and calculated intensities was very promising.

Refinement of Parameters.- A two dimensional Fourier projection along the cube axis was first made to determine the atomic positions, Fig. 2. The proper signs for the observed structure factors were determined on the basis of the parameter values obtained from the two dimensional Patterson, P (xy), Fig. 1. In addition, a synthetic Fourier projection was made to correct

for non-termination of series errors. As a result of this correction, the atoms were placed in the following positions in space group Fm3m:

(add 000; $\frac{1}{2}\frac{1}{2}$0; $\frac{1}{2}$0$\frac{1}{2}$; 0$\frac{1}{2}\frac{1}{2}$)

24 (e) Th at x00; 0x0; 00x; $\bar{x}$00; 0$\bar{x}$0; 00$\bar{x}$; with x = 0.203

 4 (b) Mn at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$

24 (d) Mn at $\frac{1}{4}\frac{1}{4}$0; $\frac{1}{4}$0$\frac{1}{4}$; 0$\frac{1}{4}\frac{1}{4}$; 0$\frac{1}{4}\frac{3}{4}$; $\frac{3}{4}$0$\frac{1}{4}$; $\frac{1}{4}\frac{3}{4}$0

32 (f) Mn at xxx; x$\bar{x}\bar{x}$; $\bar{x}$x$\bar{x}$; $\bar{x}\bar{x}$x $\bar{x}\bar{x}\bar{x}$; $\bar{x}$xx; x$\bar{x}$x; xx$\bar{x}$
with x = 0.378

32 (f) Mn at xxx; x$\bar{x}\bar{x}$; $\bar{x}$x$\bar{x}$; $\bar{x}\bar{x}$x; $\bar{x}\bar{x}\bar{x}$; $\bar{x}$xx; x$\bar{x}$x; xx$\bar{x}$
with x = 0.178.

With these parameters, the correlation factor, R, was found to be 0.20 for all reflections even though absorption and temperature corrections were not yet made.

The crystal used for intensity data was approximately circular in cross section with a radius of 0.01 cm. Bradley's data (1935) were used to obtain an absorption correction for the equitorial reflections (for our crystal, μr = 27 for copper irradiation), and it was found empirically that the equitorial corrections for a given $\sin^2\theta$ could be applied, with notable improvement, to reflections on higher layer lines.

A temperature factor of the form exp $(-B \sin^2\theta/\lambda^2)$ was used, where B , determined empirically, was 2.8 $\mathring{A}^2$. With these absorption and temperature factors, R dropped to 0.10 (Table IV).

The structure determination seems to require 24 Th and 92 Mn per unit, giving a composition Th_6Mn_{23}, rather than $ThMn_4$. This

Table IV

Calculated and Observed Structure Factors for Th_6Mn_{23}

(Corrected for Temperature and Absorption)

	$F_{calcd.}$	$F_{obsd.}$
(000)	(+ 446)	---
(200)	-----	---
(400)	+ 128	112
(600)	+ 156	180
(800)	+ 105	104
(10·00)	+ 150	115
(12·00)	+ 69	68
(14·00)	+ 48	62
(16·00)	+ 138	102
(220)	− 22	0
(420)	+ 31	27
(620)	− 18	0
(820)	− 5	0
(10·20)	+ 43	36
(12·20)	− 51	50
(14·20)	+ 41	45
(440)	+ 208	218
(640)	+ 74	66
(840)	+ 38	42
(10·40)	+ 84	88
(12·40)	+ 72	80
(14·40)	+ 87	93
(660)	+ 101	101
(860)	− 22	0
(10·60)	+ 93	82
(12·60)	+ 32	31
(14·60)	+ 35	35
(880)	+ 75	76
(10·80)	+ 51	49
(12·80)	− 43	40
(10·10·0)	+ 113	119
(12·10·0)	+ 30	33

Table IV (Continued)

	$F_{calcd.}$	$F_{obsd.}$
(111)	------	---
(311)	-----	---
(511)	+ 115	130
(711)	- 39	40
(911)	+ 21	26
(11·11)	+ 39	38
(13·11)	+ 8	0
(15·11)	+ 41	37
(331)	- 75	96
(531)	- 17	0
(731)	- 64	66
(931)	+ 28	28
(11·31)	- 47	45
(13·31)	- 54	48
(15·31)	+ 27	24
(551)	+ 104	108
(751)	+ 29	25
(951)	+ 82	77
(11·51)	+ 50	46
(13·51)	+ 5	0
(15·51)	+ 77	63
(771)	- 84	97
(971)	- 22	26
(11·71)	- 18	28
(13·71)	- 37	32
(991)	+ 43	45
(11·91)	+ 27	28
(13·91)	+ 22	27
(222)	- 114	116
(422)	- 88	79
(622)	- 18	0
(822)	- 153	148
(10·22)	+ 4	0
(12·22)	- 101	121
(14·22)	- 24	29

Table IV (Continued)

	$F_{calcd.}$		$F_{obsd.}$
(442)	−	9	0
(642)	−	13	0
(842)	−	65	69
(10·42)	+	19	16
(12·42)	−	55	59
(14·42)	−	1	0
(662)	−	9	0
(862)	−	47	59
(10·62)	+	40	38
(12·62)	−	80	69
(14·62)	+	40	33
(882)	−	111	1C5
(10·82)	+	20	20
(12·82)	+	98	98
(10·102)	+	68	69
(12·102)	−	35	32
(333)	−	183	193
(533)	+	21	21
(733)	−	136	136
(933)	−	97	112
(11·33)	−	26	13
(13·33)	−	83	100
(15·33)	−	47	48
(553)	+	49	38
(753)	−	52	44
(953)	+	35	34
(11·53)	−	7	0
(13·53)	+	4	0
(773)	−	109	115
(973)	−	39	46
(11·73)	−	77	92
(13·73)	−	96	94

Table IV (Continued)

	$F_{calcd.}$	$F_{obsd.}$
(444)	+ 57	68
(644)	+ 40	40
(844)	+ 79	83
(10·44)	+ 77	79
(12·44)	- 7	0
(14·44)	+ 39	53
(664)	+ 19	0
(864)	+ 3	0
(10·64)	+ 58	27
(12·64)	- 27	27
(884)	- 49	44
(10·84)	+ 18	21
(12·84)	+ 15	11
(10·10·4)	+ 82	94
(555)	+ 177	173
(755)	+ 31	28
(955)	+ 66	70
(11·55)	+ 104	102
(13·55)	+ 59	66
(775)	- 29	37
(975)	+ 32	40
(11·75)	- 5	0
(995)	+ 107	112
(11·95)	+ 26	29
(666)	+ 86	95
(866)	- 45	67
(10·66)	+ 83	93
(886)	- 33	40

is in quite satisfactory agreement with analytical and density data ($\rho_{calcd.}$, 9.03 gm/cc vs. $\rho_{obsd.}$, 9.02 gm/cc). The only other possibilities involve adding 4 Mn at 000 etc., in the centers of the octahedra of thorium atoms, or leaving out the 4 Mn in 4 (b). These alternatives are made doubtful by packing considerations. The Th-Mn distance would be only 2.51 $\overset{o}{A}$ for a manganese at the center of the thorium octahedron, compared with 2.82 $\overset{o}{A}$ for the sum of the single bond covalent radii, as given by Pauling (1947). On the other hand, the hole at 4 (b), at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ etc., resulting from leaving out manganese at these positions seems entirely too large. It must be admitted, however, that on the basis of intensity data alone, approximately the same agreement is obtained whatever is done with these special positions, involving only four manganese atoms.

Discussion

In Th_6Mn_{23} thorium octahedra are arranged in a face-centered array, each octahedron being surrounded by forty-four manganese atoms to form the complex polyhedron shown in Fig. 3. It is to be noted that if there is no manganese atoms at the center of the thorium octahedron this structure is unusual in that clusters of the large atoms, rather than individual large atoms, are surrounded by the small atoms. The number of manganese about the octahedron is, however, in good agreement with a rule due to Harker (1950), which assumes a closest packing of the small spheres over the surface area of the large ones. If R is the radius of a

large metal atom and r the radius of a small metal atom, the coordination number of the small atoms about the large atoms should be approximately $3(R + r)^2/r^2$. Using Pauling's CN12 radii (1947) for thorium and manganese, 1.795 and 1.306 Å respectively, and making the reasonable assumption that the average radius of a thorium octahedron is equal to the diameter of a thorium atom, the expected coordination about the octahedron is $3(4.896)^2/(1.306)^2 = 42.3$ manganese, versus 44 observed.

The polyhedra of manganese about the thorium octahedra share faces in the packing, but four holes per unit cell are left. These are presumably filled by manganese atoms in the 4 (b) positions. This gives a region between polyhedra in which there is a body-centered arrangement of manganese atoms.

From distances in Table V and Pauling's rules and radii (1947) the metallic valence of thorium and manganese are, for Th, 4.87 versus an expected 4, for Mn_I, 2.5, for Mn_{II}, 3.06, for Mn_{III}, 4.22, and Mn_{IV}, 3.42. Metallic valences of 4.16 and 5.78 are given by Pauling for manganese. The calculated valence for thorium is somewhat high, and the manganese valence is even lower than the lower valence given by Pauling. Agreement with Pauling's rule is unimpressive.

Overall, the distances average out to give good agreement with Mehl's modification of Vegard's law and Harker's simple rule, so that we can consider distances to be normal on the average. The clustering of thorium atoms, the shorter than

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expected thorium-manganese and the longer than average manganese-
manganese distances indicate that some factor is promoting
thorium binding at the expense of manganese binding.

Table V
Interatomic Distances in Th_6Mn_{23}

Th	4 Th	3.59 Å
	4 Mn	3.08
	4 Mn	3.16
	4 Mn	3.18
Mn_I(1/2 1/2 1/2), etc.	6 Th	3.71
	8 Mn	2.64
Mn_{II}(0.378 0.378 0.378), etc.	3 Th	3.08
	3 Mn	2.69
	3 Mn	2.73
	3 Mn	3.05
	1 Mn	2.64
Mn_{III}(0.178 0.178 0.178), etc.	3 Th	3.16
	3 Mn	2.55
	3 Mn	2.56
	3 Mn	2.69
Mn_{IV}(1/4 1/4 0), etc.	4 Th	3.18
	4 Mn	2.56
	4 Mn	2.73

The Structure of $ThMn_{12}$

Unit Cell and Space Group.- Powder data indicated a compound in the region of 92 atomic % manganese, and single crystals of the compound were found in an alloy of about this composition.

Single crystal data were obtained with a Buerger precession camera, M = 30°, magnification factor = 5.50 and a voltage and current regulated G. E. XRD-3 unit using Mo Kα radiation (λ = 0.7107 Å). The crystals were found to be tetragonal a_o = 8.74 ± 0.01, c_o = 4.95 ± 0.01 Å. Precession about c_o gave nets of $C4\ell$ symmetry in all levels, while precession about a_o gave nets of $C2\ell$ symmetry in all levels. The Laue symmetry is, therefore, D4h. Reflections were absent unless $h + k + \ell$ = 2n, and no other systematic absences were found. The space group is, consequently, D_{2d}^9- $I\bar{4}m2$, D_{2d}^{11} - $I\bar{4}2m$, C_{4v}^9 - $I4mm$, D_4^9 - $I42$ or D_{4h}^{17} - $I4/mmm$.

Composition of the Phase.- The body-centered lattice requires an even number of both thorium and manganese atoms per unit. The observed density, 8.12 g/cc., and approximate composition allow only two thorium atoms per unit cell. From the volume of the unit cell, 378 $Å^3$, and the atomic volumes of thorium and manganese, the number of manganese per unit cell is either 24 or 26. With 26 manganese per unit cell, two would have to be placed in two-fold positions, and they would have to be placed with thorium atoms along the four-fold axis in all space groups except $I\bar{4}m2$. This axis, 4.95 Å, is so much shorter than twice the sum of the CN 12 radii for thorium and manganese,

6.10 $\overset{\text{o}}{\text{A}}$, as to eliminate this possibility. Consequently, there

must be but 24 manganese atoms per unit cell since the eight-fold

and sixteen-fold positions of space group D_{2d}^{9} - $I\bar{4}m2$ are incom-

patible with Patterson projections. (See below.)

Atomic Positions.- Without loss of generality thorium atoms

may be placed at 000, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. All combinations of four-fold sets

place manganese atoms too close together, so that they must be

placed in 8-fold or 16-fold positions.

The Patterson projection onto (001), Fig. 4, shows major

peaks at $(\frac{1}{4}\frac{1}{4})$, $(x_1 0)$ and $(x_2 0)$. These must be due to thorium-

manganese interactions. The peak occurring at $(\frac{1}{4}\frac{1}{4})$ on P (xy) is

also at $(\frac{1}{4}\frac{1}{4})$ on the P (yz) projection, suggesting that 8 Mn are in

the parameterless set, 8 (f), found only in $I4/mmm$. There are

obviously two other parameters, each associated with one other

8-fold set, and since both occur on axes rather than diagonals

in the (001) projection, the 8-fold sets must be chosen from

8 (i) and 8 (j) of $I4/mmm$. There is no indication of the need

for z-parameters, and consequently no indication of need to

choose a lower space group than $I4/mmm$. It is not possible to

place both 8-fold sets in 8 (i) or both in 8 (j), because of

space, so 8 (i) plus 8 (j) must be used. Parameters, x = 0.361

for 8 (i) and x = 0.278 for 8 (j), are given by the (001)

Patterson, and provide for reasonable distances in the crystal.

Refinement of Parameters.- Two different methods were used

to refine the parameter values. The first method involved the

use of a synthetic Fourier projection to determine the parameter

shift due to series termination errors in the original Fourier

projection. An independent refinement, by the least squares method of Hughes (1941), was also made.

Fourier Method.- A two dimensional Fourier projection perpendicular to c_O was first made to determine the atomic positions, Fig. 5. The proper signs for the observed structure factors were determined on the basis of the parameter values obtained from the (001) Patterson projection. The Fourier parameters were $x_i = 0.361$, $x_j = 0.279$.

On the basis of the positions of these atoms, structure factors for all observed reflections were calculated. A temperature factor, $\exp(-B\sin^2\theta/\lambda^2)$, where $B = 3.5$ $\overset{O}{A}{}^2$, was applied to all the calculated structure factors and a synthetic Fourier projection was then made with these calculated data. This synthetic projection shifted the parameters slightly. For set 8 (i), x_i was 0.3605, and for set 8 (j), x_j was 0.281. On the basis of this shift, the parameter values assigned to the manganese atoms were $x_i = 0.361$ and $x_j = 0.277$.

Method of Least Squares.- The observational equations chosen for least squares refinement were of the form

$$\sum_{i=1}^{2} \left(\sqrt{w_{hk0}} \; \frac{\partial |F_{hk0}| \; \text{calcd.}}{\partial x_i} \right) \Delta x_i = \sqrt{w_{hk0}} \left(|F_{hk0}| \, \text{obsd.} - |F_{nk0}| \, \text{calcd.} \right)$$
$$= \sqrt{w_{hk0}} \; \Delta F_{nk0}$$

where the Δx_i's are the corrections to be solved for and added to the values of x_i used to obtain the quantities $|F_{hk0}|$ calcd. and w_{hk0} is a weighting factor. The $|F_{hk0}|$ calcd. were

corrected by a temperature factor similar to that used in the Fourier method. The weighting factor, w_{hk0}, was taken proportional to $1/F^2_{hk0}$ for F's greater than two times the minimum observed F and proportional to $1/4 F^2_{min}$ for F's smaller than $2F_{min}$.

The normal equations for Δx_1 and Δx_2 are

$$D_{11} \Delta x_1 + D_{12} \Delta x_2 = A_1$$

$$D_{21} \Delta x_1 + D_{22} \Delta x_2 = A_2$$

where $D_{ij} = \sum_{hk0} \left(\sqrt{w_{hk0}} \; \frac{\partial |F_{hk0}| \text{ calcd.}}{\partial x_i} \right) \left(\sqrt{w_{hk0}} \; \frac{\partial |F_{hk0}| \text{ calcd.}}{\partial x_j} \right)$

$A_1 = \sum_{hk0} \left(\sqrt{w_{hk0}} \; \frac{\partial |F_{hk0}| \text{ calcd.}}{\partial x_1} \right) \left(\sqrt{w_{hk0}} \; \Delta F_{hk0} \right)$

$A_2 = \sum_{hk0} \left(\sqrt{w_{hk0}} \; \frac{\partial |F_{hk0}| \text{ calcd.}}{\partial x_2} \right) \left(\sqrt{w_{hk0}} \; \Delta F_{hk0} \right)$

Using the (hk0) precession data with initial parameter values of $x_1 = 0.361$ and $x_j = 0.278$, the value of $\Delta x_1 = + 0.0019$ and $\Delta x_j = - 0.0039$. This then gives parameter values of $x_1 = 0.363$ and $x_j = 0.274$. If we neglect reflections (400), (660), and (880), which appear to be abnormally influenced by extinction and absorption, we obtain corrections $\Delta x_1 = - 0.0017$ and $\Delta x_j = - 0.0008$, yielding parameter values of $x_1 = 0.359$ and $x_2 = 0.277$.

The expression used for the standard error of a parameter was

$$\sigma_i = \sqrt{\frac{\sum_{hk0} w_{hk0} \Delta F^2_{hk0}}{m - s}} \; D^{-1}_{ii}$$

where $\underline{m}$ is the number of observational equations, $\underline{s}$ is the number of parameters, and D_{ii}^{-1} is the ith diagonal element of the matrix inverse to that of D_{ii}. Since the off diagonal matrix element is relatively small, we can write as an approximation that

$$D_{ii}^{-1} \simeq \frac{1}{\sum_{hk0} W_{hk0} \left(\frac{\partial |F_{hk0}|_{calcd.}}{\partial x_i} \right)^2}.$$

This gives a standard error of 0.0023 for $x_i = 0.361$ and of 0.0021 for $x_j = 0.277$. From the two sets of parameters arrived at by the least squares method, the following seem to be the best parameter values, $x_i = .361 \pm .002$ and $x_j = .277 \pm .002$.

On the basis of the Fourier and least squares methods, the atoms were placed in the following positions in D_{4h}^{17}:

(add 000, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ to all positions)

2 (a) Th at 000

8 (f) Mn at $\frac{1}{4}\frac{1}{4}\frac{1}{4}$; $\frac{3}{4}\frac{3}{4}\frac{1}{4}$; $\frac{1}{4}\frac{3}{4}\frac{1}{4}$; $\frac{3}{4}\frac{1}{4}\frac{1}{4}$

8 (i) Mn at x00; $\bar{x}$00; 0x0; 0$\bar{x}$0

with x = 0.361

8 (j) Mn at x$\frac{1}{2}$0; $\bar{x}\frac{1}{2}$0; $\frac{1}{2}$x0; $\frac{1}{2}\bar{x}$0

with x = 0.277.

The observed and calculated structure factors are given in Table VI. The correlation factor, R, was found to be 0.10.

Table VI

Calculated and Observed Structure Factors for $ThMn_{12}$

	$F_{calcd.}$	$F_{obsd.}$
(000)	(+ 780)	---
(200)	+ 66	64
(400)	+ 409	352
(600)	+ 120	129
(800)	+ 322	324
(10·00)	+ 70	83
(12·00)	+ 187	193
(110)	+ 80	---
(310)	+ 133	158
(510)	+ 170	181
(710)	− 4	0
(910)	+ 120	107
(11·10)	+ 73	88
(220)	+ 133	117
(420)	− 80	73
(620)	+ 163	173
(820)	+ 9	0
(10·20)	+ 101	104
(330)	+ 189	191
(530)	+ 206	204
(730)	+ 39	0
(930)	+ 151	138
(11·30)	+ 100	104
(440)	+ 222	211
(640)	+ 5	0
(840)	+ 216	219
(10·40)	− 12	0
(550)	+ 218	192
(750)	+ 66	51
(950)	+ 171	170
(11·50)	+ 120	98

Table VI (Continued)

	$F_{calcd.}$	$F_{obsd.}$
(660)	+ 184	143
(860)	+ 54	0
(10·60)	+ 130	147
(770)	− 52	0
(880)	+ 225	286
(002)	+ 291	294
(004)	+ 399	331
(006)	+ 142	153
(101)	+ 88	96
(103)	+ 77	0
(105)	+ 65	0
(202)	+ 339	340
(204)	+ 56	0
(206)	+ 191	176
(301)	+ 247	278
(303)	+ 194	168
(305)	+ 151	112
(402)	+ 117	106
(404)	+ 272	273
(406)	+ 81	0
(501)	+ 103	95
(503)	+ 90	0
(505)	+ 77	86
(602)	+ 310	296
(604)	+ 97	79

Table VI (Continued)

	$F_{calcd.}$	$F_{obsd.}$
(701)	+ 102	129
(703)	+ 94	77
(705)	+ 83	89
(802)	+ 139	147
(804)	+ 267	301
(901)	+ 58	0
(903)	+ 55	83
(10·02)	+ 216	270
(11·01)	+ 152	196

Table VII

Interatomic Distances in $ThMn_{12}$

Th	4 Mn	3.15 A
	8 Mn	3.15 A
	8 Mn	3.33 A
Mn_I(1/4 1/4 1/4), etc.	4 Mn	2.53 A
	4 Mn	2.70 A
	2 Th	3.33 A
	2 Mn	2.48 A
Mn_{II}(.361 0 0), etc.	4 Mn	2.70 A
	2 Mn	2.76 A
	2 Mn	2.73 A
	4 Mn	3.02 A
	1 Th	3.15 A
	1 Mn	2.42 A
Mn_{III}(1/2 .279 0), etc.	2 Th	3.15 A
	4 Mn	2.53 A
	2 Mn	2.76 A
	2 Mn	2.73 A
	2 Mn	2.73 A

Discussion

In $ThMn_{12}$ each thorium atom is surrounded by twenty manganese atoms, twelve at 3.15 Å, eight at a somewhat larger distance, 3.33 Å (Fig. 6). By Harker's rule, above, a coordination number of 16.8 is predicted, and the higher coordination probably results from the larger distances to eight of the atoms. A complete table of interatomic distances is given in Table VII.

There is considerable similarity in the structure of Th_6Mn_{23} and $ThMn_{12}$. In both cases body-centered cubes of manganese atoms tie thorium atoms together. In Th_6Mn_{23} each such cube has a thorium atom attached to each face, while in $ThMn_{12}$ only two opposite faces are bound to thorium.

Pauling's radii and rules lead to metallic valences of 4.67 for Th, 4.40 for Mn_I, 3.17 for Mn_{II} and 4.24 for Mn_{III}, in fair agreement with an expected valence of 4 for Th, and Pauling's lower valence for manganese 4.16.

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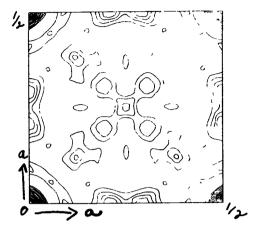
Fig. 1. Patterson projection of Th_6Mn_{23} onto (001).
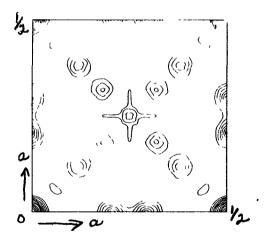
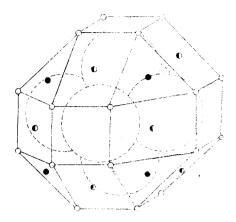Fig. 2. Electron-density projection of Th_6Mn_{23} onto (001).

Fig. 3. Packing of manganese atoms about thorium
octahedra; Th atoms, large dotted circles;
Mn_{II}, small unshaded circles; Mn_{III}, small
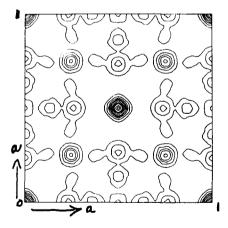shaded circles; Mn_{IV}, small half shaded
circles.

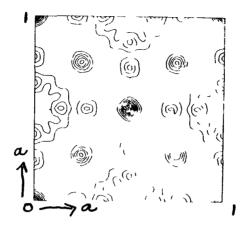Fig. 4. Patterson projection of $ThMn_{12}$ onto (001).

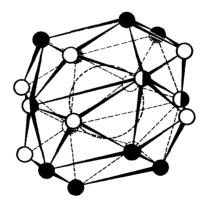Fig. 5. Electron-density projection of $ThMn_{12}$ onto (001).

Fig. 6. Packing of manganese atoms about thorium; Th atom, large dotted circle; Mn_I, small unshaded circles; Mn_{II}, small half-shaded circles; Mn_{III}, small shaded circles.