Table 3. *Constitution of the potash–soda felspars*

	Microline	Anorthoclase		Moonstone
		Rim	Core	
Percentage of the constituent felspars as determined by the X-ray method	I′. K-rich 82 % II′. Na-rich 18 %	I″. K-rich 71 % II″. Na-rich 29 %	I″. K-rich 50 % II″. Na-rich 21 % III″. Na-rich 29 % } 50 %	I‴. K-rich 42 % II‴—V‴. Na-rich 58 %
Ratio of Or- to Ab-molecules as calculated from chemical analysis	77 : 23	74 : 26	49 : 51	41 : 59
Twinning of the constituent felspars	Albite (II′)	Albite (II″)	Albite (II″) Pericline (III″)	Pericline (III‴—V‴)

soda felspars as the only counterpart products of the potash felspar in the process of exsolution.

It is interesting to note that in the pericline-twinned felspars the (direct) γ angle and in the albite-twinned felspars the (reciprocal) γ^* angle have persistently been found to be 90°, irrespective of the nature of the mother felspar—microcline, anorthoclase or moonstone—from which they have been produced upon exsolution. This is natural, for pericline twinning has the (direct) b axis and albite twinning the (reciprocal) b^* axis as the twin axis. The ease with which polysymmetric synthesis takes place in a triclinic crystal when one of its direct zone angles is 90° has already been instanced in the wollastonite group of minerals (Ito, 1950, p. 101). The foregoing examples have shown that a similar statement is applicable to the reciprocal angles.

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Compounds of Thorium with Transition Metals. I. The Thorium–Manganese System*

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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 $MgZn_2$ ($C14$-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

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Table 1. *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)			ThCo[b]	ThNi[b]	
	$ThMn_2(C14)$[d]	$ThFe_3$[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]	Th_2Fe_{17}[b]	Th_2Co_{17}[b]	Th_2Ni_{17}[b]	

a (Baenziger, 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 nickel compound.

of intermetallic compounds of thorium with the transition metals.

Like uranium (Baenziger, Rundle, Snow & Wilson, 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 1.

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.

Owing 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 % manganese were examined. All the samples were analyzed chemically within an accuracy of 1% or better.

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 % 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.

$ThMn_2$

Powder data and single-crystal data taken with a Buerger precession camera, Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å), $\mu = 30°$, and a magnification factor of 5·5, were obtained. The latter data included precession about the hexagonal axis, [10.0] and [21.0]. Both powder and precession diagrams require a hexagonal lattice,

$$a_0 = 5{\cdot}48 \pm 0{\cdot}01,\ c_0 = 8{\cdot}95 \pm 0{\cdot}02\ \text{Å}\,.$$

Precession diagrams about c_0 exhibited $C6l$ symmetry in all levels, while the [10.0] and [21.0] 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 $MgZn_2$ ($C14$ structure type). Structure factors calculated for the ideal structure,

$$\begin{aligned}&4\,\mathrm{Th}\ \text{at}\ \pm(\tfrac{1}{3}, \tfrac{2}{3}, z);\ \pm(\tfrac{2}{3}, \tfrac{1}{3}, \tfrac{1}{2}+z);\ z = \tfrac{1}{16},\\ &2\,\mathrm{Mn}\ \text{at}\ 000;\ 00\tfrac{1}{2},\\ &6\,\mathrm{Mn}\ \text{at}\ \pm(x, 2x, \tfrac{1}{4});\ \pm(2\bar{x}, \bar{x}, \tfrac{1}{4});\ \pm(x, \bar{x}, \tfrac{1}{4});\ x = -\tfrac{1}{6},\end{aligned}$$

were compared with structure factors obtained from timed exposures using the precession camera. The calculated and observed structure factors are given in Table 2. The correlation factor,

$$R = \Sigma||F_o| - |F_c|| \div \Sigma|F_o|$$

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

$$F_{(11\cdot6)} > 4{\cdot}4F_{(11\cdot4)},\ F_{(22\cdot2)} > 4{\cdot}4F_{(11\cdot4)},\ \text{and}\ F_{(11\cdot6)} \cong F_{(22\cdot2)}\,.$$

Table 2. *Calculated and observed structure factors for* $ThMn_2$

	F_c	F_o
(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
(0,0,10)	−173	207
(112)	+274	282
(114)	0	0
(116)	−112	100
(118)	−204	214
(1,1,10)	− 93	117
(222)	+112	100
(224)	+ 91	105
(226)	−185	187
(228)	−112	171
(332)	+174	163

Table 3. *Interatomic distances in* $ThMn_2$

Th	4 Th	3·35 Å
	12 Mn	3·21
Mn_I (0, 0, 0), etc.	6 Th	3·21
	6 Mn	2·74
Mn_{II} $(\frac{1}{3}, \frac{1}{6}, \frac{1}{4})$, etc.	6 Th	3·21
	6 Mn	2·74

These reflections occur at nearly the same sin θ and should have very similar temperature and adsorption corrections in the technique employed. From these it can be shown that $z_{Th} = 0{\cdot}0625 \pm 0{\cdot}002$. A Fourier projection on to (00·1) led to a manganese parameter of 0·167, ideal within our observation.

From interatomic distances in Table 3 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 6·08 for thorium and 2·58 for manganese. These 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.

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

$$a_0 = 12{\cdot}523 \pm 0{\cdot}001 \text{ Å}$$

as determined using a cylindrical back-reflection powder camera of 5·0 cm. radius and the method of Jette & Foote (1935).

The multiple-film technique of Robertson (1943) was used to obtain rotation and zero-level Weissenberg diagrams for rotation about a fourfold axis. Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ 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–$F\bar{4}3m$, 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 $9{\cdot}02 \pm 0{\cdot}05$ g.cm.$^{-3}$. 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 or 96 manganese per unit cell. Assuming Mehl's modification of Vegard's law (Mehl & Mair, 1928) to apply, and taking the atomic volume of thorium as 32·8 Å^3 and that of manganese as 12·4 Å^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 $F\bar{4}3m$. In addition, 24 (*f*) of $F\bar{4}3m$ is equivalent to 24 (*e*) of the other two groups.* The twenty-four thoriums are almost certainly in one of these sets, since combinations of four-, eight- and sixteen-fold sets include a number of parameterless sets, and are easily eliminated. The parameterless set, 24 (*d*), is incompatible with the X-ray data, while the stronger peaks on the Patterson,

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

$P(x, y)$, 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, $P(x, y, 0)$, 24 (e) requires peaks on the diagonal at $(x, x, 0)$, 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, $P(x, y)$, 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 corresponding positions in $F43$. These 48-fold sets are eliminated by consideration of the two-dimensional Patterson, $P(x, y)$, together with the Patterson section, $P(x, y, \frac{12}{60})$, 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 $P(x, y, \frac{12}{60})$. The only other 48-fold sets, 48 (g) of $Fm3m$ or 48 (i) of $F43$, require Th–Mn peaks on $P(x, y)$ at $(\frac{1}{4}, \frac{1}{4})$, $(\frac{1}{4}, x)$ and $(\frac{1}{4}, \frac{3}{60})$. Though some indication of peaks, with $x = \frac{8}{60}$, are found, these are so far from the expected magnitudes that this possibility seemed unpromising.

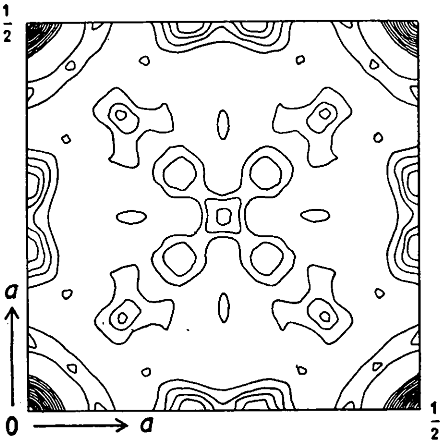

Fig. 1. Patterson projection of Th_6Mn_{23} onto (001).

Turning to 32-fold sets, it was found that by placing 64 manganese atoms in 32 (f) of $Fm3m$ or $F43$, with $x_1 = \frac{11}{60}$, $x_2 = \frac{23}{60}$, 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 $(\frac{1}{4}, \frac{8}{60})$. These positions are all found in $Fm3m$ and $F43$, and are permitted in $F\bar{4}3m$ 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 $z = 0, \frac{3}{60}, \frac{7}{60}, \frac{12}{60}, \frac{14}{60}$ and $\frac{15}{60}$, 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, $P(x, y)$, 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 $Fm3m$:

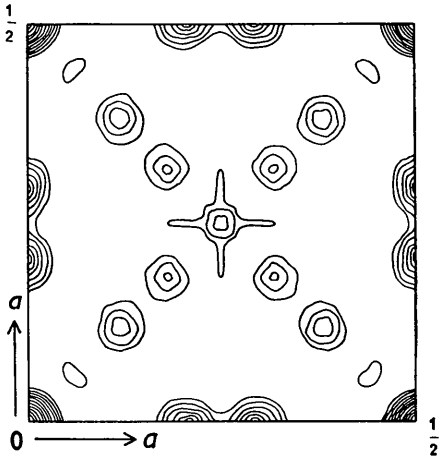

Fig. 2. Electron-density projection of Th_6Mn_{23} onto (001).

(add $0, 0, 0;\ \frac{1}{2}, \frac{1}{2}, 0;\ \frac{1}{2}, 0, \frac{1}{2};\ 0, \frac{1}{2}, \frac{1}{2}$)
24 (e) Th at $x, 0, 0;\ 0, x, 0;\ 0, 0, x;\ \bar{x}, 0, 0;\ 0, \bar{x}, 0;$
$0, 0, \bar{x};$ with $x = 0{\cdot}203$.
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 $x, x, x;\ x, \bar{x}, \bar{x};\ \bar{x}, x, \bar{x};\ \bar{x}, \bar{x}, x;\ \bar{x}, \bar{x}, \bar{x};$
$\bar{x}, x, x;\ x, \bar{x}, x;\ x, x, \bar{x};$ with $x{=}0{\cdot}378$.
32 (f) Mn at $x, x, x;\ x, \bar{x}, \bar{x};\ \bar{x}, x, \bar{x};\ \bar{x}, \bar{x}, x;\ \bar{x}, \bar{x}, \bar{x};$
$\bar{x}, x, x;\ x, \bar{x}, x;\ x, x, \bar{x};$ with $x{=}0{\cdot}178$.

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 equatorial reflections

Table 4. *Calculated and observed structure factors for* Th_6Mn_{23}

(Corrected for temperature and absorption)

	F_c	F_o
(000)	(+446)	—
(200)	—	—
(400)	+128	112
(600)	+156	180
(800)	+105	104
(10,0,0)	+150	115
(12,0,0)	+69	68
(14,0,0)	+48	62
(16,0,0)	+138	102
(220)	−22	0
(420)	+31	27
(620)	−18	0
(820)	−5	0
(10,2,0)	+43	36
(12,2,0)	−51	50
(14,2,0)	+41	45
(440)	+208	218
(640)	+74	66
(840)	+38	42
(10,4,0)	+84	88
(12,4,0)	+72	80
(14,4,0)	+87	93
(660)	+101	101
(860)	−22	0
(10,6,0)	+93	82
(12,6,0)	+32	31
(14,6,0)	+35	35
(880)	+75	76
(10,8,0)	+51	49
(12,8,0)	−43	40
(10,10,0)	+113	119
(12,10,0)	+30	33
(111)	—	—
(311)	—	—
(511)	+115	130
(711)	−39	40
(911)	+21	26
(11,1,1)	+39	38
(13,1,1)	+8	0
(15,1,1)	+41	37
(331)	−75	96
(531)	−17	0
(731)	−64	66
(931)	+28	28
(11,3,1)	−47	45
(13,3,1)	−54	48
(15,3,1)	+27	24
(551)	+104	108
(751)	+29	25
(951)	+82	77
(11,5,1)	+50	46
(13,5,1)	+5	0
(15,5,1)	+77	63
(771)	−84	97
(971)	−22	26
(11,7,1)	−18	28
(13,7,1)	−37	32
(991)	+43	45
(11,9,1)	+27	28
(13,9,1)	+22	27

Table 4 (*cont.*)

	F_c	F_o
(222)	−114	116
(422)	−88	79
(622)	−18	0
(822)	−153	148
(10,2,2)	+4	0
(12,2,2)	−101	121
(14,2,2)	−24	29
(442)	−9	0
(642)	−13	0
(842)	−65	69
(10,4,2)	+19	16
(12,4,2)	−55	59
(14,4,2)	−1	0
(662)	−9	0
(862)	−47	59
(10,6,2)	+40	38
(12,6,2)	−80	69
(14,6,2)	+40	33
(882)	−111	105
(10,8,2)	+20	20
(12,8,2)	+98	98
(10,10,2)	+68	69
(12,10,2)	−35	32
(333)	−183	193
(533)	+21	21
(733)	−136	136
(933)	−97	112
(11,3,3)	−26	13
(13,3,3)	−83	100
(15,3,3)	−47	48
(553)	+49	38
(753)	−52	44
(953)	+35	34
(11,5,3)	−7	0
(13,5,3)	+4	0
(773)	−109	115
(973)	−39	46
(11,7,3)	−77	92
(13,7,3)	−96	94
(444)	+57	68
(644)	+40	40
(844)	+79	83
(10,4,4)	+77	79
(12,4,4)	−7	0
(14,4,4)	+39	53
(664)	+19	0
(864)	+3	0
(10,6,4)	+58	27
(12,6,4)	−27	27
(884)	−49	44
(10,8,4)	+18	21
(12,8,4)	+15	11
(10,10,4)	+82	94
(555)	+177	173
(755)	+31	28
(955)	+66	70
(11,5,5)	+104	102
(13,5,5)	+59	66

Table 4 (*cont.*)

	F_c	F_o
(775)	− 29	37
(975)	+ 32	40
(11,7,5)	− 5	0
(995)	+107	112
(11,9,5)	+ 26	29
(666)	+ 86	95
(866)	− 45	67
(10,6,6)	+ 83	93
(886)	− 33	40

(for our crystal, $\mu r = 27$ for copper irradiation), and it was found empirically that the equatorial 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 Å². With these absorption and temperature factors, R dropped to 0·10 (Table 4).

The structure determination seems to require 24 Th and 92 Mn per unit, giving a composition Th_6Mn_{23}, rather than $ThMn_4$. This is in quite satisfactory agreement with analytical and density data ($\varrho_c = 9{\cdot}03$ g.cm.$^{-3}$ *v.* $\varrho_o = 9{\cdot}02$ g.cm.$^{-3}$). The only other possibilities involve adding 4 Mn at 0, 0, 0 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 Å for a manganese at the center of the thorium octahedron, compared with 2·82 Å 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 are 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 C.N. 12 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 $3(4{\cdot}896)^2/(1{\cdot}306)^2 = 42{\cdot}3$ manganese, *v.* 44 observed.

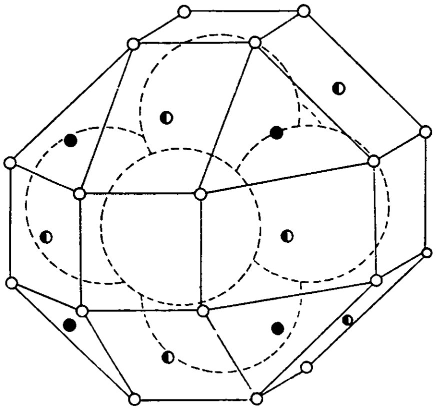

Fig. 3. Packing af manganese atoms about thorium octahedra in Th_6Mn_{23}.
Large broken circles: Th.
Small unshaded circles: Mn_{II}.
Small shaded circles: Mn_{III}.
Small half-shaded circles: Mn_{IV}.

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 5 and Pauling's rules and radii (1947) the metallic valence of thorium and manganese are, for Th, 4·87 *v.* an expected 4; for Mn_I, 2·5; for Mn_{II}, 3·06; for Mn_{III}, 4·22; and for 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.

Table 5. *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 ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), 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} ($\frac{1}{4}$, $\frac{1}{4}$, 0), etc.	4 Th	3·18
	4 Mn	2·56
	4 Mn	2·73

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 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.

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, $\mu=30°$, magnification factor=5·50 and a voltage and current regulated G.E. XRD-3 unit using Mo $K\alpha$ radiation (λ = 0·7107 Å). The crystals were found to be tetragonal,

$$a_0 = 8{\cdot}74 \pm 0{\cdot}01,\ c_0 = 4{\cdot}95 \pm 0{\cdot}01 \text{ Å} .$$

Precession about c_0 gave nets of $C4l$ symmetry in all levels, while precession about a_0 gave nets of $C2l$ symmetry in all levels. The Laue symmetry is, therefore, D_{4h}. Reflections were absent unless $h+k+l=2n$, and no other systematic absences were found. The space group is, consequently, $D_{2d}^{9}\text{–}I\bar{4}m2$, $D_{2d}^{11}\text{–}I\bar{4}2m$, $C_{4v}^{9}\text{–}I4mm$, $D_{4}^{9}\text{–}I42$ or $D_{4h}^{17}\text{–}I4/mmm$.

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.cm.$^{-3}$, 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 twofold positions, and they would have to be placed with thorium atoms along the fourfold 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 C.N. 12 radii for thorium and manganese, 6·10 Å, as to eliminate this possibility. Consequently, there must be but 24 manganese atoms per unit cell since the eightfold and sixteenfold positions of space group $D_{2d}^{9}\text{–}I\bar{4}m2$ are incompatible with Patterson projections (see below).

Atomic positions

Without loss of generality, thorium atoms may be placed at 0, 0, 0; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. All combinations of fourfold 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 $P(x, y)$ is also at $(\frac{1}{4}, \frac{1}{4})$ on the $P(y, z)$ 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.

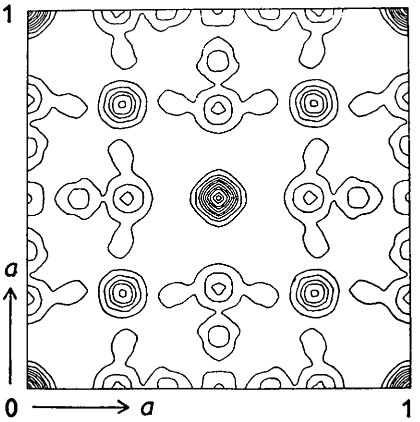

Fig. 4. Patterson projection of $ThMn_{12}$ onto (001).

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_0 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 Å^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.

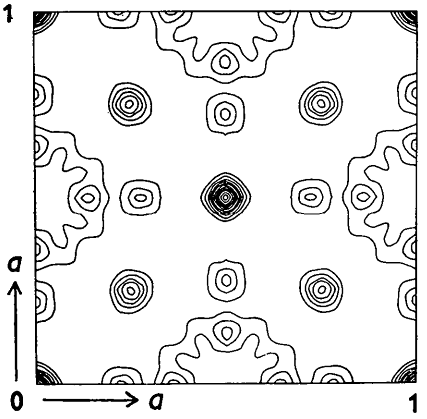

Fig. 5. Electron-density projection of $ThMn_{12}$ onto (001).

On the basis of this shift, the parameter values assigned to the manganese atoms were $x_i = 0{\cdot}361$ and $x_j = 0{\cdot}277$.

Method of least squares

The observational equations chosen for least-squares refinement were of the form

$$\sum_{i=1}^{2}\left(\sqrt{\omega_{hk0}}\,\frac{\delta|F_{hk0}|_c}{\delta x_i}\right)\Delta x_i = \sqrt{\omega_{hk0}}\cdot(|F_{hk0}|_o-|F_{hk0}|_c)$$
$$= \sqrt{\omega_{hk0}}\cdot\Delta F_{hk0}\,,$$

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

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

$$D_{ij} = \sum_{hk0}\left(\sqrt{\omega_{hk0}}\,\frac{\delta|F_{hk0}|_c}{\delta x_i}\right)\left(\sqrt{\omega_{hk0}}\,\frac{\delta|F_{hk0}|_c}{\delta x_j}\right),$$

$$A_1 = \sum_{hk0}\left(\sqrt{\omega_{hk0}}\,\frac{\delta|F_{hk0}|_c}{\delta x_1}\right)(\sqrt{\omega_{hk0}}\cdot\Delta F_{hk0})\,,$$

$$A_2 = \sum_{hk0}\left(\sqrt{\omega_{hk0}}\,\frac{\alpha|F_{hk0}|_c}{\delta x_2}\right)(\sqrt{\omega_{hk0}}\cdot\Delta F_{hk0})\,.$$

Using the (*hk*0) precession data with initial parameter values of $x_i = 0{\cdot}361$ and $x_j = 0{\cdot}278$, the value of Δx_i is $+0{\cdot}0019$ and of Δx_j is $-0{\cdot}0039$. This then gives parameter values of $x_i = 0{\cdot}363$ and $x_j = 0{\cdot}274$. If we neglect reflections (400), (660) and (880), which appear to be abnormally influenced by extinction and absorption, we obtain corrections $\Delta x_i = -0{\cdot}0017$ and $\Delta x_j = -0{\cdot}0008$, yielding parameter values of $x_i = 0{\cdot}359$ and $x_j = 0{\cdot}277$.

The expression used for the standard error of a parameter was

$$\sigma_i = \sqrt{\left(\frac{\sum\limits_{hk0}\omega_{hk0}\Delta F^2_{hk0}}{m-s}\,D^{-1}_{ii}\right)},$$

where m is the number of observational equations, s is the number of parameters, and D^{-1}_{ii} 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

$$D^{-1}_{ii} \cong \frac{1}{\sum\limits_{hk0}\omega_{hk0}\left(\dfrac{\delta|F_{hk0}|_c}{\delta x_i}\right)^2}\,.$$

This gives a standard error of 0·0023 for $x_i = 0{\cdot}361$ and of 0·0021 for $x_j = 0{\cdot}277$. From the two sets of parameters arrived at by the least-squares method, the following seem to be the best parameter values, $x_i = 0{\cdot}361 \pm 0{\cdot}002$ and $x_j = 0{\cdot}277 \pm 0{\cdot}002$.

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

(add 0, 0, 0; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ to all positions)
2 (*a*) Th at 0, 0, 0.
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 $x, 0, 0$; $\bar{x}, 0, 0$; $0, x, 0$; $0, \bar{x}, 0$;
with $x = 0{\cdot}361$.
8 (*j*) Mn at $x, \frac{1}{2}, 0$; $\bar{x}, \frac{1}{2}, 0$; $\frac{1}{2}, x, 0$; $\frac{1}{2}, \bar{x}, 0$;
with $x = 0{\cdot}277$.

The observed and calculated structure factors are given in Table 6. The correlation factor, R, was 0·10.

Table 6. *Calculated and observed structure factors for* $ThMn_{12}$

	F_c	F_o
(000)	(+780)	—
(200)	+ 66	64
(400)	+409	352
(600)	+120	129
(800)	+322	324
(10,0,0)	+ 70	83
(12,0,0)	+187	193
(110)	+ 80	—
(310)	+133	158
(510)	+170	181
(710)	− 4	0
(910)	+120	107
(11,1,0)	+ 73	88
(220)	+133	117
(420)	− 80	73
(620)	+163	173
(820)	+ 9	0
(10,2,0)	+101	104
(330)	+189	191
(530)	+206	204
(730)	+ 39	0
(930)	+151	138
(11,3,0)	+100	104

Table 6 (*cont.*)

	F_c	F_o
(440)	+222	211
(640)	+ 5	0
(840)	+216	219
(10,4,0)	− 12	0
(550)	+218	192
(750)	+ 66	51
(950)	+171	170
(11,5,0)	+120	98
(660)	+184	143
(860)	+ 54	0
(10,6,0)	+130	147
(770)	− 52	0
(880)	+225	286
(002)	+291	294
(004)	+399	331
(006)	+162	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
(701)	+102	129
(703)	+ 94	77
(705)	+ 83	89
(802)	+139	147
(804)	+267	301
(901)	+ 58	0
(903)	+ 55	83
(10,0,2)	+216	270
(11,0,1)	+152	196

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 7.

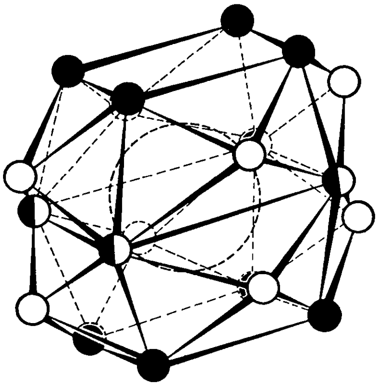

Fig. 6. Packing of manganese atoms about thorium in $ThMn_{12}$.
Large broken circle: Th.
Small unshaded circles: Mn_{I}.
Small half-shaded circles: Mn_{II}.
Small shaded circles: Mn_{III}.

Table 7. *Interatomic distances in* $ThMn_{12}$

Th	4 Mn	3·15 Å
	8 Mn	3·15
	8 Mn	3·33
Mn_{I} (¼, ¼, ¼), etc.	4 Mn	2·53
	4 Mn	2·70
	2 Th	3·33
	2 Mn	2·48
Mn_{II} (0·361, 0, 0), etc.	4 Mn	2·70
	2 Mn	2·76
	2 Mn	2·73
	4 Mn	3·02
	1 Th	3·15
	1 Mn	2·42
Mn_{III} (½, 0·279, 0), etc.	2 Th	3·15
	4 Mn	2·53
	2 Mn	2·76
	2 Mn	2·73
	2 Mn	2·73

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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