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COMPOUNDS OF THORIUM WITH TRANSITION METALS OF THE FIRST PERIOD

by

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Approved:

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TABLE OF CONTENTS

INTRODUCTION

The chemistry and metallurgy of thorium have been investigated extensively at the Ames Laboratory during the past few years. One of the fields of particular interest has been the binary alloy systems of thorium with the transition elements.

The composition of intermetallic compounds, such as $ThMn_2$, Th_6Mn_{23}, $ThMn_{12}$, et cetera, bears in general little relation to the customary valences of the metals. The significant factors, which at present are only partially understood, are the ratio of valence electrons to atomic nuclei, relative values of metallic radii, and differences in electronegativity of combining atoms.

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 (1), thorium forms no compounds with chromium and 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. Structures of the manganese compounds differ from those of iron, cobalt, and nickel compounds, which are very similar. A summary of the known compounds, stable at room temperature, is given in Table I.

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]	
					$Th_2Cu(CuAl_2)$[d]
(None)			$ThCo$[b]	$ThNi$[b]	
	$ThMn_2(MgZn_2)$	$ThFe_3$[b,c]	$ThCo_{2-3}$[b,c]	$ThNi_2(AlB_2)$	$ThCu_2(AlB_2)$[e]
	Th_6Mn_{23}[b]				$ThCu_4$[f]
		$ThFe_5(CaZn_5)$	$ThCo_5(CaZn_5)$	$ThNi_5(CaZn_5)$	
		Th_2Fe_{17}[b]	Th_2Co_{17}[b]	Th_2Ni_{17}[b]	
	$ThMn_{12}$[b]				

[a] Structure determined by Baenziger (2).

[b] New structural type.

[c] Structure not yet fully known.

[d] Structure reported by Rundle (3).

[e] Structure reported by Rundle (4).

[f] Compound reported by Grube and Boltzenhardt (5).

EXPERIMENTAL PROCEDURE

Preparation and Analyses of Binary Alloys

The samples were prepared by fusing thorium metal and the transition element in a vacuum or under an inert stmosphere. After cooling, samples were prepared for powder diagrams by reducing the alloy to a fine powder in a diamond mortar and then annealing the powder at 500 - 600 °C for several hours. Single crystals were selected from the bulk sample with the aid of a small microscope. The alloys were chemically analyzed for their thorium and transition element content to within an accuracy of 1-3 per cent by weight.

X-ray Diffraction Data

For purposes of identification, X-ray powder diagrams were taken with a Debye-Scherrer camera of radius 5.73 centimeters. A cylindrical back-reflection camera of 5.0 centimeters radius was used to determine precise lattice constants. For single crystal work, both a Buerger precession camera and a Weissenberg camera of 2.836 centimeters radius were used.

Nickel filtered Cu Ka radiation ($\lambda = 1.5418\mathring{A}$) from a Philips diffraction unit was used with the powder and Weissenberg cameras. Single crystal data were obtained with the Buerger precession camera using zirconium filtered Mo Kα radiation ($\lambda = 0.7107\text{Å}$) from a voltage and current regulated General Electric XRD-3 unit.

The intensities of the observed ($hk\ell$) reflections were estimated visually. The multiple film technique of Robertson (6) was used to obtain rotation and n-level Weissenberg diagrams. The precession data were obtained from timed exposures with a film factor of two.

The $|F_{hk\ell}|^2$ and $F_{hk\ell}$ in the Patterson and electron density projections were determined from the intensities by the following formula,

$$|F_{hk\ell}|^2 \propto I_{obs.}/(L.P.)(T)(A)$$

where F_{hkl} is the structure factor for the ($hk\ell$) reflection, I_{obs}, the observed intensity, L.P., the Lorentz and polarization factor, T, the temperature correction, and A, the absorption correction. The Lorentz-polarization factor for rotation and zero layer Weissenberg diagrams is equal to $\frac{1 + \cos^2 2\theta}{\sin 2\theta}$. For the precession diagrams, this factor was obtained from a paper by Evans, Tilden and Hughes (7). Only in a few cases were temperature and absorption corrections required. An isotropic temperature factor of the form, $\exp(-B \sin^2\theta/\lambda^2)$, where B is an empirically determined constant, was then applied to the observed intensities. The absorption corrections were based on Bradley's data (8).

Use of Fourier Series in Crystal Analyses

As the electron density in a crystal varies periodically along any direction through the lattice, it is possible to describe the electron distribution by a Fourier series. The electron density at any point within the unit cell, ρ (xyz), is then represented by the Fourier series

$$\rho\,(xyz) = \frac{1}{V} \sum_{h=-\infty}^{+\infty} \sum_{k=-\infty}^{+\infty} \sum_{\ell=-\infty}^{+\infty} F_{hk\ell}\, e^{2\pi i(hx + ky + \ell z)}$$

where V is the volume of the unit cell.

By projecting the electron density in the unit cell parallel to the C_0 axis onto the (001) plane, for example, the Fourier series can be greatly simplified. The resulting function is

$$\rho\,(xy) = \frac{1}{A} \sum_{h=-\infty}^{+\infty} \sum_{k=-\infty}^{+\infty} F_{hko}\, e^{2\pi i(hx + ky)},$$

where A is the area of the unit cell face on which the projection is made.

A later development by Patterson (9) in the use of Fourier series, involving $|F_{hk\ell}|^2$, has found wide usage in solving complex structures. The function, P(xyz), represented by the series

$$P(xyz) = \sum_{h=-\infty}^{+\infty} \sum_{k=-\infty}^{+\infty} \sum_{\ell=-\infty}^{+\infty} |F_{hk\ell}|^2\, e^{2\pi i(hx+ky+\ell z)},$$

defines an electron-density product that has maxima at distances and directions from the origin corresponding to the distances and directions between pairs of atoms in the crystal. The amplitudes of the peaks of P(xyz) correspond to the products of the electron densities at the two points considered. By projecting P(xyz) along the c_0 axis onto the (001) plane, we obtain the simplified function,

$$P(xy) = \sum_{h=-\infty}^{+\infty} \sum_{k=-\infty}^{+\infty} |F_{hko}|^2 \, e^{2\pi i(hx + ky)} .$$

Methods of Computation

The projections involving Fourier series were carried out by two different methods dependent upon the complexity of the series. Where the number of terms in the series were few, the strip method of summation by Beevers and Lipson (10) was used. For the more complex Fourier syntheses, the summations were carried out on an International Business Machine Tabulator using punched cards (11).

THE THORIUM-MANGANESE SYSTEM

Introduction

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 one per cent 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 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.

Structure of $ThMn_2$

Unit cell and space group

Powder data and single crystal data taken with a Buerger precession camera, Mo Kα radiation ($\lambda = 0.7107 \text{Å}$), $\mu = 30°$, 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, $a_0 = 5.48 \pm 0.01$ Å, $c_0 = 8.95 \pm 0.02$ Å. Precession diagrams about c_0 exhibited $C6\ell$ symmetry in all levels, while the [10·0] and [21·0] diagrams possessed $C2\ell$ 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.

Composition of the phase

From the powder data the approximate composition appears to be 67 atomic per cent manganese. Using the method of atomic volumes in which we assume the validity of Mehl's modification of Vegard's law (12), we find that the volume of a unit cell containing four $ThMn_2$ molecules should be 230.4 Å^3 where the atomic volume of thorium is assumed equal to 32.8 Å^3 and that of manganese equal to 12.4 Å^3. This agrees very well with the volume of the unit cell, 232.8 Å^3, calculated from the lattice constants.

<u>Atomic positions</u>

This phase, occurring at approximately 67 atomic per cent manganese, had an axial ratio and symmetry suggesting that it was isomorphous with $MgZn_2$. Structure factors calculated for the ideal structure,

4 Th at $\pm$ (1/3 2/3 z); $\pm$ (2/3 1/3 1/2 + z) with z = 1/16
2 Mn(I) at 000; 00 1/2
6 Mn(II) at $\pm$ (x 2x 1/4); $\pm$ ($2\bar{x}$ $\bar{x}$ 1/4);
$\pm$ (x $\bar{x}$ 1/4) with x = -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, $R = \sum \big| |F_{obsd.}| - |F_{calcd.}| \big| / \sum |F_{obsd.}|$ was 0.13 for (HK·L) data.

Table II. Calculated and Observed Structure Factors for $ThMn_2$

	$F_{calcd.}$	$F_{obsd.}$		$F_{calcd.}$	$F_{obsd.}$
(100)	- 97	106	(002)	+ 144	104
(200)	- 162	180	(004)	+ 142	138
(300)	+ 252	231	(006)	- 229	190
(400)	- 121	150	(008)	- 122	107
(500)	- 68	40	(0•0•$\underline{10}$)	- 173	207
(600)	+ 159	183			
			(112)	+ 274	282
(110)	+ 296	322	(114)	0	0
(120)	- 85	90	(116)	- 112	100
(130)	- 78	70	(118)	- 204	214
(140)	+ 204	193	(1•1•$\underline{10}$)	- 93	117
(150)	- 65	41			
			(222)	+ 112	100
(220)	+ 338	336	(224)	+ 91	105
(230)	- 72	57	(226)	- 185	187
(240)	- 106	80	(228)	- 112	171
(250)	+ 174	142			
			(332)	+ 174	163
(330)	+ 184	197			
(340)	- 62	50			

Refinement of parameters

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 $F_{(11\cdot6)} > 4.4\ F_{(11\cdot4)}$, $F_{(22\cdot2)} > 4.4\ F_{(11\cdot4)}$ and $F_{(11\cdot6)} \cong F_{(22\cdot2)}$. These reflections occur at nearly the same sin Θ, and should have very similar temperature and adsorption corrections in the technique employed. From calculations shown in Table III it can be seen that $z_{Th} = 0.0625 \pm 0.002$. A Fourier projection onto (00·1) led to a manganese x parameter of 0.167, ideal within our observation.

Table III. Refinement of Thorium z Parameter

Reflection	z	A_{Th}	A_{Mn}	F_{hk}
(114)	.0625	0	0	0
	.060	+ 16	0	+ 16
	.058	+ 29	0	+ 29
	.056	+ 42	0	+ 42
	.054	+ 55	0	+ 55
(116)	.0625	- 163	+ 51	- 112
	.060	- 147	+ 51	- 96
	.058	- 133	+ 51	- 82
	.056	- 118	+ 51	- 67
	.054	- 103	+ 51	- 52
(222)	.0625	+ 163	- 51	+ 112
	.060	+ 168	- 51	+ 117
	.058	+ 171	- 51	+ 120
	.056	+ 175	- 51	+ 124
	.054	+ 179	- 51	+ 128

Discussion

In $ThMn_2$ each thorium atom is surrounded by twelve manganese atoms at the corners of a truncated tetrahedron (Figure 1). The thorium atom is also bonded tetrahedrally to four thorium atoms through the hexagonal faces of the truncated

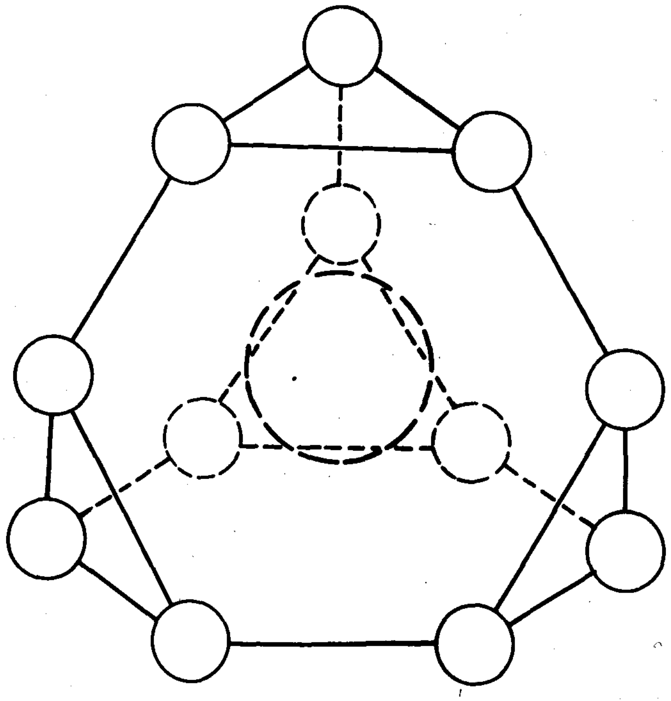

Figure 1. Packing of manganese atoms about thorium in $ThMn_2$; thorium atom, large dotted circle; manganese atoms, small circles.

tetrahedron. A complete summary of interatomic distances is given in Table IV.

Table IV. Interatomic Distances in $ThMn_2$

Th	4 Th	3.35 Å
	12 Mn	3.21 Å
Mn(I)	6 Th	3.21 Å
	6Mn	2.74 Å
Mn(II)	6 Th	3.21 Å
	6 Mn	2.74 Å

Structure of Th_6Mn_{23}

Unit cell and space group

An alloy with 81.8 atomic per cent 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 $a_0 = 12.523 \pm 0.001$ Å as determined using a cylindrical back-reflection powder camera of 5.0 centimeters radius and the method of Jette and Foote (14).

The multiple film technique of Robertson (6) 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 centimeters were employed.

Absences characteristic of a face-centered lattice were the only ones noted. Only those ($hk\ell$) reflections were present for which h, k, and ℓ were either all even or all odd. 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 per cent 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, or 96 manganese atoms per unit cell. Assuming Mehl's modification of Vegard's law (12) 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 (15, I, p.363) and F43 (15, I, p.340), and 24 (g) of $F\bar{4}3m$ (15, I, p.325). In addition, 24 (f) of $F\bar{4}3m$ is equivalent to 24 (e). 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, P(xy), Figure 2, 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 (xx0), 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), Figure 2. 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 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(xy), together 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 (1/4 1/4), (1/4 x) and (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-dimensional Patterson projection, Figure 2, is accounted for except by what we believe to be a diffraction ring around the origin, and a very small peak at (1/4 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, 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, Figure 3. 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), Figure 2. 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; 1/2 1/2 0; 1/2 0 1/2; 0 1/2 1/2)
24: (e) Th at x00; 0x0; 00x; $\bar{x}00$; $0\bar{x}0$; $00\bar{x}$
with x = 0.203 ± .001.
4: (b) Mn(I) at 1/2 1/2 1/2.
24: (d) Mn(II) at 1/4 1/4 0; 1/4 0 1/4; 0 1/4 1/4;
0 1/4 3/4; 3/4 0 1/4; 1/4 3/4 0.

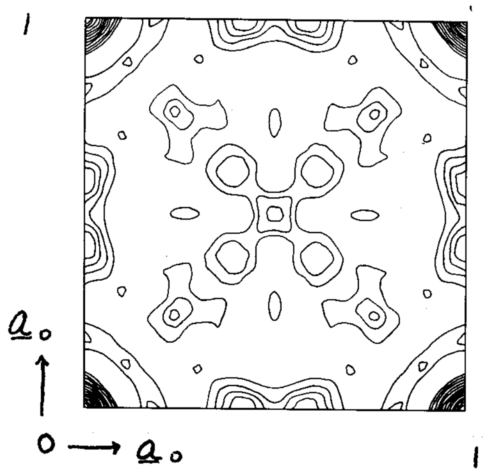

Figure 2. Patterson projection of Th_6Mn_{23} onto (001).

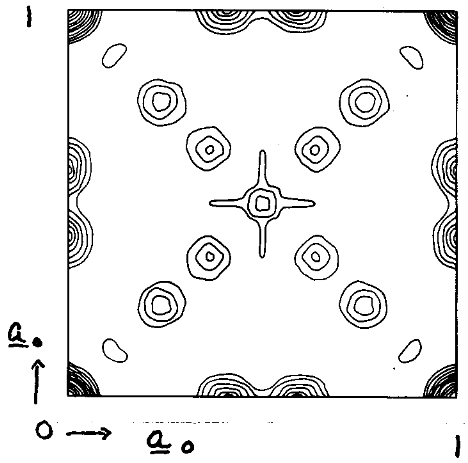

Figure 3. Electron-density projection of Th_6Mn_{23} onto (001).

32: (f) Mn(III) 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 $x = 0.378 \pm .002$.

32: (f) Mn(IV) 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 $x = 0.178 \pm .0025$.

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 centimeter. Bradley's data (8) were used to obtain an absorption correction for the equatorial reflections (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 Å^2. With these absorption and temperature factors, R dropped to 0.10 as given in Table V.

Estimation of the magnitude of the above errors in the thorium and manganese parameters is based on a modification of Cruikshank's method (16) as applied to two-dimensional electron density maps. The standard deviation, $\sigma(x)$, in the parameter, x, is defined as follows,

$$\sigma(x) = \frac{\sigma(A_h)}{A_{hh}}$$

$$\sigma(x) = \frac{2\pi}{Aa_0}\left[\sum_{-\infty}^{+\infty}\sum_{-\infty}^{+\infty}(h+k)^2\ m\Delta F^2\right]^{1/2}\frac{\partial^2\rho}{\partial x^2}$$

where σ is standard deviation of an error, ρ is electron density, a_0 is unit-cell axis, A is area of electron density map, A_h is $\frac{\partial\rho}{\partial x}$, A_{hh} is $\partial^2\rho/\partial x^2$, h and k are Miller indices, m is structure factor multiplicity, and F is the structure factor. These deviations are listed in the above point groups.

The structure determination seems to require 24 Th and 92 Mn per unit cell, giving a composition Th_6Mn_{23}, rather than $ThMn_4$. This is in quite satisfactory agreement with analytical and density data ($\rho_{calcd.}$, 9.03 gm/cc versus $\rho_{obsd.}$, 9.02 gm/cc). The only other possibilities involve adding 4 Mn at 000, et cetera, 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 (13). On the other hand, the hole at 4 (b), at 1/2 1/2 1/2, et cetera, resulting from leaving out manganese at these positions seems entirely too large. It must be admitted, however, that on the basis of intensity data

Table V. Calculated and Observed Structure Factors for Th_6Mn_{23}

(Corrected for Temperature and Absorption)

	$F_{calcd.}$	$F_{obsd.}$		$F_{calcd.}$	$F_{obsd.}$
(000)	(+ 446)	---	(511)	+ 115	130
(200)	-----	---	(711)	- 39	40
(400)	+ 128	112	(911)	+ 21	26
(600)	+ 156	180	(11•1•1)	+ 39	38
(800)	+ 105	104	(13•1•1)	+ 8	0
(10•0•0)	+ 150	115	(15•1•1)	+ 41	37
(12•0•0)	+ 69	68			
(14•0•0)	+ 48	62	(331)	- 75	96
(16•0•0)	+ 138	102	(531)	- 17	0
			(731)	- 64	66
(220)	- 22	0	(931)	+ 28	28
(420)	+ 31	27	(11•3•1)	- 47	45
(620)	- 18	0	(13•3•1)	- 54	48
(820)	- 5	0	(15•3•1)	+ 27	24
(10•2•0)	+ 43	36			
(12•2•0)	- 51	50	(551)	+ 104	108
(14•2•0)	+ 41	45	(751)	+ 29	25
			(951)	+ 82	77
(440)	+ 208	218	(11•5•1)	+ 50	46
(640)	+ 74	66	(13•5•1)	+ 5	0
(840)	+ 38	42	(15•5•1)	+ 77	63
(10•4•0)	+ 84	88			
(12•4•0)	+ 72	80	(771)	- 84	97
(14•4•0)	+ 87	93	(971)	- 22	26
			(11•7•1)	- 18	28
(660)	+ 101	101	(13•7•1)	- 37	32
(860)	- 22	0			
(10•6•0)	+ 93	82	(991)	+ 43	45
(12•6•0)	+ 32	31	(11•9•1)	+ 27	28
(14•6•0)	+ 35	35	(13•9•1)	+ 22	27
(880)	+ 75	76	(222)	- 114	116
(10•8•0)	+ 51	49	(422)	- 88	79
(12•8•0)	- 43	40	(622)	- 18	0
			(822)	- 153	148
(10•10•0)	+ 113	119	(10•2•2)	+ 4	0
(12•10•0)	+ 30	33	(12•2•2)	- 101	121
			(14•2•2)	- 24	29
(111)	-----	---			
(311)	-----	---			

Table V. Continued

	$F_{\text{calcd.}}$	$F_{\text{obsd.}}$		$F_{\text{calcd.}}$	$F_{\text{obsd.}}$
(442)	- 9	0	(14•4•4)	+ 39	53
(642)	- 13	0			
(842)	- 65	69	(664)	+ 19	0
(10•4•2)	+ 19	16	(864)	+ 3	0
(12•4•2)	- 55	59	(10•6•4)	+ 58	27
(14•4•2)	- 1	0	(12•6•4)	- 27	27
(662)	- 9	0	(884)	- 49	44
(862)	- 47	59	(10•8•4)	+ 18	21
(10•6•2)	+ 40	38	(12•8•4)	+ 15	11
(12•6•2)	- 80	69			
(14•6•2)	+ 40	33	(10•10•4)	+ 82	94
(882)	- 111	105	(555)	+ 177	173
(10•8•2)	+ 20	20	(755)	+ 31	28
(12•8•2)	+ 98	98	(955)	+ 66	70
			(11•5•5)	+ 104	102
(10•10•2)	+ 68	69	(13•5•5)	+ 59	66
(12•10•2)	- 35	32			
			(775)	- 29	37
(333)	- 183	193	(975)	+ 32	40
(533)	+ 21	21	(11•7•5)	- 5	0
(733)	- 136	136			
(933)	- 97	112	(995)	+ 107	112
(11•3•3)	- 26	13	(11•9•5)	+ 26	29
(13•3•3)	- 83	100			
(15•3•3)	- 47	48	(666)	+ 86	95
			(866)	- 45	67
(553)	+ 49	38	(10•6•6)	+ 83	93
(753)	- 52	44			
(953)	+ 35	34	(886)	- 33	40
(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			

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 44 manganese atoms to form the complex polyhedron shown in Figure 4. A summary of interatomic distances is listed in Table VI. 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 atoms about the octahedron is, however, in good agreement with Harker's rule (17), which assumes a closest packing of the small spheres over the surface areas 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 (13) 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 octahderon is $3(4.896)^2/(1.306)^2 = 42.3$ manganese,

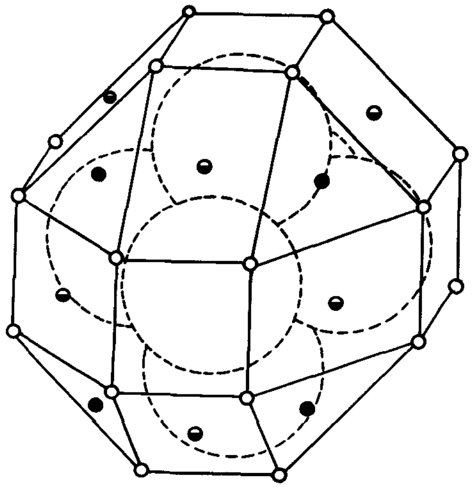

Figure 4. Packing of manganese atoms about thorium octahedra in Th_6Mn_{23}; thorium atoms, large dotted circles; manganese (II) small unshaded circles; manganese (III), small shaded circles; manganese (IV), small half-shaded circles.

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.

Table VI. Interatomic Distances in Th_6Mn_{23}

Th	4 Th	3.59 Å
	4 Mn	3.08 Å
	4 Mn	3.16 Å
	4 Mn	3.18 Å
	6 Mn	3.71 Å
Mn(I)	6 Th	3.71 Å
	8 Mn	2.64 Å
Mn(II)	4 Th	3.18 Å
	4 Mn	2.56 Å
	4 Mn	2.73 Å
Mn(III)	3 Th	3.08 Å
	3 Mn	2.69 Å
	3 Mn	2.73 Å
	3 Mn	3.05 Å
	1 Mn	2.64 Å
Mn(IV)	3 Th	3.16 Å
	3 Mn	2.55 Å
	3 Mn	2.56 Å
	3 Mn	2.69 Å

Structure of $ThMn_{12}$

Unit Cell and space group

Powder data indicated a compound in the region of 92 atomic per cent 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 General Electric XRD-3 unit using Mo Kα radiation ($\lambda = 0.7107$ Å). The crystals were found to be tetragonal with $a_0 = 8.74 \pm 0.01$ Å and $c_0 = 4.95 \pm 0.01$ Å. Precession about c_0 gave nets of $C4\ell$ symmetry in all levels, while precession about a_0 gave nets of $C2\ell$ symmetry in all levels. The Laue symmetry is, therefore, D_{4h}. 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 cell. The observed density, 8.12 g/cc., and approximate composition allow only two thorium atoms per unit cell. From the volumes of thorium and manganese, the number of manganese atoms per unit cell is either 24 or 26. With 26 manganese atoms 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 CN12 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 eight-fold and 16-fold positions of space group D_{2d}^{9} - $I\bar{4}m2$ are incompatible with Patterson projections.

<u>Atomic positions</u>

Without loss of generality thorium atoms may be placed at 000, 1/2 1/2 1/2. All combinations of four-fold sets place manganese atoms too close together, so that they must be placed in eight-fold or 16-fold positions.

The Patterson projection onto (001), Figure 5, shows major peaks at (1/4 1/4), (x_1 0) and (x_2 0). These must be due to thorium-manganese interactions. The peak occurring at (1/4 1/4) on P(xy) is also at (1/4 1/4) on the P(yz) projection, suggesting that 8 Mn are in the parameterless set, 8 (f), found only in I4/mmm (15, I, p.225). There are obviously two other parameters, each associated with one other eight-fold set, and since both occur on axes rather than diagonals in the (001) projection, the eight-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 the need to choose a lower space group than I4/mmm. It is not possible to place both eight-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 (18), was also made.

A two-dimensional Fourier projection perpendicular to $\underline{c}_0$ was made to determine the atomic positions, Figure 6. 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

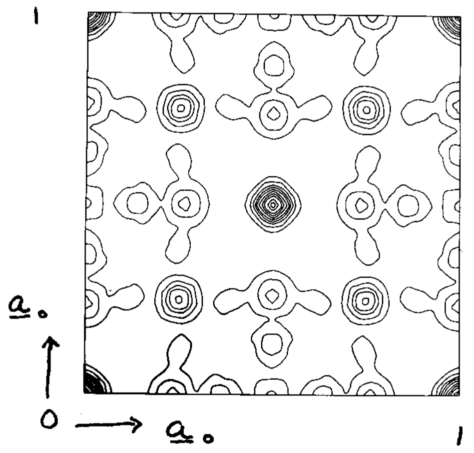

Figure 5. Patterson projection of $ThMn_{12}$ onto (001).

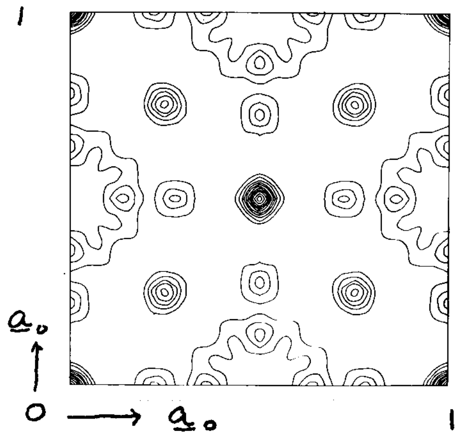

Figure 6. Electron-density projection of $ThMn_{12}$ onto (001).

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. On the basis of this shift, the parameter values assigned to the manganese atoms were $x_i = 0.361$ and $x_j = 0.277$.

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

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

$$= \sqrt{\omega_{hk0}} \, (|F_{hk0}| \text{ obsd.} - |F_{hk0}| \text{ calcd.})$$

$$= \sqrt{\omega_{hk0}} \, \Delta F_{hk0}$$

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 $|F_{hk0}|$calcd., and ω_{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, ω_{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 $x_i = 0.361$ and $x_j = 0.278$, the value of $\Delta x_i = + 0.0019$ and $\Delta x_j = - 0.0039$. This then gives parameter values of $x_i = 0.363$ 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 $\Delta x_i = - 0.0017$ 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

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

where m is the number of observational equations, s is the number of parameters, and D_{ii}^{-1} is the i^{th} 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

$$D_{ii}^{-1} \cong \frac{1}{\sum_{hk0} \omega_{hk0} \left(\frac{\partial |F_{hk0}|\ \text{calcd.}}{\partial x_i} \right)^2} .$$

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; 1/2 1/2 1/2)

2: (a) Th at 000.

8: (f) Mn(I) at 1/4 1/4 1/4; 3/4 3/4 1/4;
1/4 3/4 1/4; 3/4 1/4 1/4.

8: (i) Mn(II) at x00; $\bar{x}$00; 0x0; 0$\bar{x}$0 with x = 0.361.

8: (j) Mn(III) at x 1/2 0; $\bar{x}$ 1/2 0; 1/2 $\bar{x}$0; 1/2 $\bar{x}$0;
with x = 0.277.

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

Table VII. 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•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
(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

	$F_{calcd.}$	$F_{obsd.}$
(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

Table VII. Continued.

	$F_{calcd.}$	$F_{obsd.}$		$F_{calcd.}$	$F_{obsd.}$
(901)	+ 58	0	(10·0·2)	+ 216	270
(903)	+ 55	83	(11·0·1)	+ 152	196

Discussion

In $ThMn_{12}$ each thorium atom is surrounded by 20 manganese atoms, 12 at 3.15 Å, and eight at a somewhat larger distance, 3.33 Å (Figure 7). By Harker's rule (17) 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 VIII.

There is considerable similarity in the structure of Th_6Mn_{23} and $ThMn_{12}$. In both cases body-centered cubes of manganese atoms, though somewhat distorted in $ThMn_{12}$, 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.

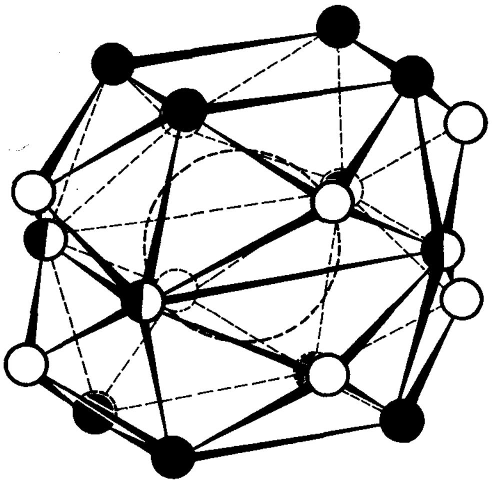

Figure 7. Packing of manganese atoms about thorium in $ThMn_{12}$; thorium atom, large dotted circle; manganese(I), small unshaded circles; manganese (II), small half-shaded circles; manganese(III), small shaded circles.

Table VIII. Interatomic Distances in $ThMn_{12}$

Th	4 Mn	3.15 Å
	8 Mn	3.15 Å
	8 Mn	3.33 Å
Mn(I)	4 Mn	2.53 Å
	4 Mn	2.70 Å
	2 Th	3.33 Å
	2 Mn	2.48 Å
Mn(II)	4 Mn	2.70 Å
	2 Mn	2.76 Å
	2 Mn	2.73 Å
	4 Mn	3.02 Å
	1 Th	3.15 Å
	1 Mn	2.42 Å
Mn(III)	2 Th	3.15 Å
	4 Mn	2.53 Å
	2 Mn	2.76 Å
	2 Mn	2.73 Å
	2 Mn	2.73 Å

THE THORIUM-IRON SYSTEM

Introduction

The initial investigation of the thorium-iron system was by means of X-ray powder data. The powder diagrams, however, were not easily interpretable due to a fogged background on the film caused by X-ray fluorscence of the sample. This diffuse scattering is strongest when the wave-length of the absorption edge of the irradiated element is slightly longer than the wave-length of the irradiating beam. The wave-length of the absorption edge of iron is not much longer than that of copper Kα, and consequently, iron-containing compounds fluorsce strongly in copper Kα radiation.

Alloys with compositions ranging from 0 to 100 atomic per cent iron were examined. All the samples were analyzed chemically within an accuracy of a few per cent or better. Aside from the elements themselves, the powder diagrams indicated the presence of four other phases with compositions of roughly 33, 70, 80, and 90 atomic per cent iron. The samples did not appear to be homogeneous. Fortunately, single crystals of the four compounds existing in these regions were obtained.

The structure of Th_7Fe_3 has been previously determined by Baenziger (2). There were not enough single crystals of the other three compounds to perform a direct chemical analysis or to run a density determination on material known to be strictly a single phase. The formulas representing the compounds $ThFe_3$, $ThFe_5$, and Th_2Fe_{17} are based upon the rough chemical compositions, atomic volumes and space group considerations.

Structure of Th_7Fe_3

The compound, Th_7Fe_3, as determined by Baenziger (2), belongs to space group C_{6v}^4 - C6mc with lattice constants $a_0 = 9.85$ Å and $c_0 = 6.15$ Å. The atomic positions are as follows:

2 Th(I) at $1/3\ 2/3\ z;\ 2/3\ 1/3\ 1/2 + z$ with $z = 0.06$.
6 Th(II) at $x\ 2x\ z;\ 2\bar{x}\ \bar{x}\ z;\ x\ \bar{x}\ z;\ \bar{x}\ x\ 1/2;\ \bar{x}\ 2\bar{x}\ 1/2 + z;$
$2x\ x\ 1/2 + z$ with $x = 0.126$ and $z = 0.250$.
6 Th(III) at same positions with $x = 0.544$ and $z = 0.03$.
6 Fe at same positions with $x = 0.815$ and $z = 0.31$.

Structure of $ThFe_3$

Unit cell and space group

Single crystals of this compound were found in an alloy of approximately 50 atomic per cent iron. Single crystal data were obtained with a Buerger precession camera, $\mu = 30°$, magnification factor of 6.00, and a voltage and current regulated General Electric XRD-3 unit using Mo Kα radiation ($\lambda = 0.7107$ Å). Data were also obtained with a Weissenberg camera of 5.73 centimeters diameter and Cu Kα radiation ($\lambda = 1.5418$ Å). The crystal was found to be hexagonal with $\underline{a}_o = 5.22$ Å and $\underline{c}_o = 24.96$ Å.

The X-ray data showed some unexplainable absences. The rotation diagram about the [21.0] direction indicated the absence of a center of symmetry, in other words, intensity $(hk\ell) \neq$ intensity $(\bar{h}\bar{k}\bar{\ell})$, except for the zero and third layer lines. This was an apparent contradiction of Friedel's Law (19), the condition that $F_{hk\ell} = F_{\bar{h}\bar{k}\bar{\ell}}$. Since the frequency of the incident radiation, Cu Kα, is very nearly equal to the critical absorption frequency of iron, we might expect such an effect. However, the precession (HO·L) data, obtained with Mo Kα radiation, also indicated the absence of a center of symmetry except for H = 3n. Thus, it is not possible to explain completely these anomalous effects at this time.

Precession about $\underline{c}_o$ indicated an apparent C6ℓ symmetry in all levels. The Laue symmetry is thus D_{6h}. The following systematic extinctions were noted:

(HK·L) none.
(HK·0) except for H - K = 3n.
(HH·L) except for L = 3n

The possible space groups are D_{6h}^1 - (6/mmm, D_6^1 - C62, D_6^4 - $C6_22$, D_6^5 - $C6_42$, C_{6v}^1 - C6mm, or D_{3h}^1 - $C\bar{6}m2$.

Composition of the phase

The powder data seemed to indicate a compound somewhere within the region 70 - 81 atomic per cent iron. Due to the systematic extinctions, it was assumed that the atoms were present in multiples of three. The compositions were then calculated, using the method of atomic volumes, on the basis of 6, 9, and 12 thorium atoms present in the unit cell. Using a unit cell volume of 589.0 Å^3, a thorium atomic volume of 32.8 Å^3, and an iron atomic volume of 11.3 Å^3, we find for

6 Th atoms, 34.7 Fe atoms (roughly $ThFe_6$),
9 Th atoms, 26.0 Fe atoms (roughly $ThFe_3$),
12 Th atoms, 17.3 Fe atoms (roughly Th_2Fe_3).

The compositions corresponding to 6 and 12 thorium atoms per unit cell appear to be highly improbable. It was therefore assumed that the formula representing this phase should be ThF_3.

Discussion

Because there was no ready interpretation of the apparent inconsistency of the data, that is, the absence of a center of symmetry in the X-ray data, no thorough structural determination was attempted. However, due to the systematic extinctions one can postulate certain relationships between the x, y, and z parameters of the atoms within the unit cell. The systematic extinctions in the (HH•L) data, with L = 3n, indicate that for every atom in the unit cell there are two of the same species separated from it by one third and two thirds of the $\underline{c}_0$ axis. The (HK•0) data with H - K = 3n are very similar to the corresponding $ThCo_{2-3}$ data and indicate that the atoms are related by rhombohedral symmetry in the x and y parameters.

Space groups D^1_{6h}, D^1_6, D^4_6, D^5_6, and C^1_{6v} can be eliminated as possibilities since they place the thorium atoms too close together by requiring two or more of them to lie in the same plane perpendicular to the $\underline{c}_0$ axis. The crystal must therefore belong to space group D^1_{3h} - C6m2.

Structure of $ThFe_5$

Single crystals of this compound were obtained from an inhomogeneous sample containing approximately 67 atomic per cent iron. Single crystal data were obtained with a Buerger precession camera, μ = 30°, magnification factor of 6.00, and a voltage and current regulated General Electric XRD-3 unit using Mo Kα radiation (λ = 0.7107 Å).

The compound appeared to be isomorphous with $CaZn_5$. It has an hexagonal unit cell with $\underline{a}_0$ = 5.13 Å and $\underline{c}_0$ = 4.02 Å. The atomic positions in space group D_{6h} -C6mmm are as follows:

1 Th at 000.

2 Fe(I) at 1/3 2/3 0; 2/3 1/3 0.

3 Fe(II) at 1/2 1/2 0; 1/2 0 1/2; 1/2 1/2 1/2.

A summary of interatomic distances is listed in Table IX.

Table IX. Interatomic Distances in $ThFe_5$

Th	6 Fe	2.96 Å
	12 Fe	3.27 Å
Fe(I)	3 Th	2.96 Å
	6 Fe	2.50 Å
Fe(II)	4 Th	3.27 Å
	4 Fe	2.57 Å
	4 Fe	2.50 Å

Structure of Th_2Fe_{17}

Unit cell and space group

Single crystals of this compound were found in an alloy of approximately 90 atomic per cent iron. Single crystal data were obtained with a Buerger precession camera, $\mu = 30°$, magnification of 6.00, and a voltage and current regulated General Electric XRD-3 unit using Mo Kα radiation ($\lambda = 0.7107$ Å). The crystal was found to be monoclinic with $\underline{a}_0 = 9.68$ Å, $\underline{b}_0 = 8.56$ Å, $\underline{c}_0 = 6.46$ Å, and $\beta = 99°\ 20'$.

Precession about $\underline{b}_0$ gave nets of $C2\ell$ symmetry in all levels. Because there was no evidence of the existence of a three-fold axis, the Laue symmetry, D_{3d}, was not considered possible. Therefore, the Laue symmetry for this crystal is C_{2h}. The only systemmatic extinctions noted were for $(hk\ell)$ data with $h + k = 2n + 1$. The allowed space groups are $C_{2h}^3 - C2/m$, $C_s^3 - Cm$, $C_2^3 - C2$.

Composition of the phase

The powder data indicated a single phase at approximately 90 atomic per cent iron. This is roughly substantiated if we use the method of atomic volumes to determine the composition. In any allowed space groups, the number of atoms present in the unit cell must be multiples of two. Using a unit cell volume of 528.2 Å^3, a thorium atomic volume of 32.8 Å^3 and an iron atomic volume of 11.3 Å^3, we find for

2 Th atoms, 41 Fe atoms (roughly $ThFe_{20}$),
4 Th atoms, 35 Fe atoms (roughly $ThFe_9$),
6 Th atoms, 30 Fe atoms (roughly $ThFe_5$).

The compositions corresponding to two and six thorium atoms per unit cell appear to be highly improbable. The actual composition, Th_2Fe_{17}, is based upon space group considerations and the similarity between this compound and the corresponding thorium-manganese and thorium-nickel compounds,

$ThMn_{12}$ and Th_2Ni_{17}. A more complete discussion of the similarity between these compounds will be found in the final discussion section.

Postulated structure

It was tentatively assumed that the crystal belonged to the space group C_{2h}^3 - C2/m. The allowed positions in C_{2h}^3 - C2/m are as follows:

(add 000; 1/2 1/2 0)

2: (a) 000. (b) 0 1/2 0. (c) 00 1/2. (d) 0 1/2 1/2.

4: (e) 1/4 1/4 0; 1/4 3/4 0. (f) 1/4 1/4 1/2; 1/4 3/4 1/2.

(g) $0y0$; $0\bar{y}0$. (h) $0y$ 1/2; $\bar{0}y$ 1/2.

(i) $x0z$; $\bar{x}0\bar{z}$.

8: (j) xyz; $x\bar{y}z$; $\bar{x}y\bar{z}$; $\bar{x}\bar{y}\bar{z}$.

A two-dimensional Patterson function, $P(xz)$, (Figure 8) was plotted. It did not seem possible to interpret the Patterson function by placing the four thorium atoms into two two-fold sets. The only apparent alternative was to place them in set 4(i) with $x \approx .167$ and $z \approx 0.333$.

The Patterson projection indicated that the thorium atoms were surrounded by hexagons of iron atoms. This suggested that there might be some relationship between this structure and $ThFe_5$. This relation is made more obvious by selecting a different, though larger, monoclinic unit cell with $\underline{a}_0' = 14.86$ Å, $\underline{b}_0' = 8.56$ Å, $\underline{c}_0' = 12.47$ Å, and $\beta' = 90°$.

In this case, $\underline{a}_o'(Th_2Fe_{17}) \approx 3\ \underline{a}_o''(ThFe_5)$, $\underline{b}_o'(Th_2Fe_{17}) \approx \sqrt{3}\ \underline{a}_o''(ThFe_5)$ and $\underline{c}_o'(Th_2Fe_{17}) \approx 3\ \underline{c}_o''(ThFe_5)$.

The arrangement of the atoms in the $ThFe_5$ lattice perpendicular to the [21.0] direction is shown in Figure 9. Knowing the relation between the original axes selected, $\underline{a}_o$ and $\underline{c}_o$, and those from the larger unit cell, $\underline{a}_o'$ and $\underline{c}_o'$, we can select a unit cell from Figure 9 which corresponds to the smaller cell. It is then apparent that the four thorium atoms within this unit cell correspond to the fourfold set, 4(i), originally selected. If we replace the two thorium atoms along the sides of the unit cell by four iron atoms, we will have a crystal composition of Th_2Fe_{17}, and if we replace them by six iron atoms, we will obtain a composition of $ThFe_9$. The number and manner of substitution is still uncertain and will require a thorough structural determination. However, from our knowledge of $ThMn_{12}$ and Th_2Ni_{17} structures, we find that usually two atoms of the transition element replace one of the thorium atoms. On this basis, we ascribe to this phase the formula Th_2Fe_{17} and postulate the following atomic positions in space group $C_{2h}^3 - C_2/m$:

4 Th in set 4(i) with x = 0.167 and z = 0.333.

8 Fe(I) in set 8(j) with x = 0.167, y = 0.360 and z = 0.333.

Figure 8. Patterson projection of Th_2Fe_{17} onto (010).

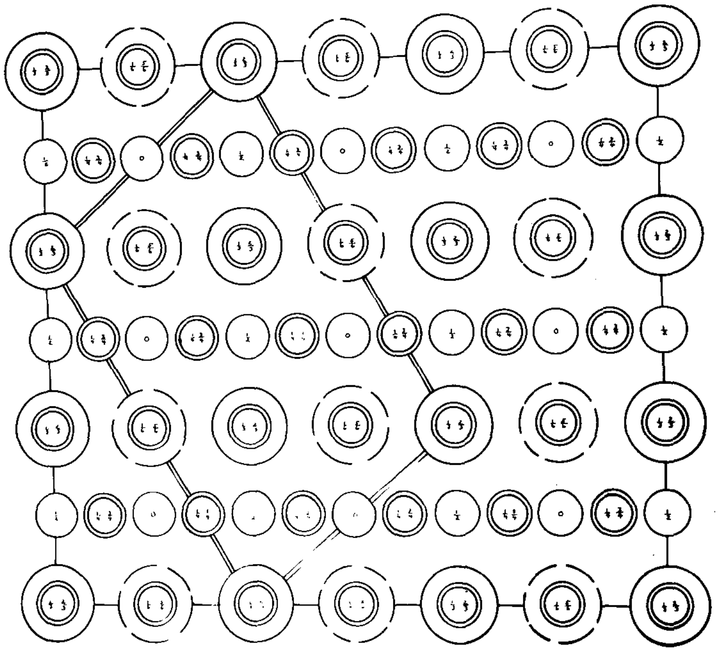

Figure 9. Projection of $ThFe_5$ lattice perpendicular to [21·0] direction and of Th_2Fe_{17} lattice onto (010) plane; double solid line, smallest possible monoclinic Th_2Fe_{17} unit cell; thorium atoms with y=0, large solid circles; thorium atoms with y=1/2, large dotted circles; iron atoms with y parameters enclosed, small circles.

8 Fe(II) in set 8(j) with $x = 0.417$, $y = 0.250$ and $z = 0.333$.

4 Fe(III) in set 4(g) with $y = 0.140$.

4 Fe(IV) in set 4(e).

4 Fe(V) in set 4(i) with $x = 0.167$ and $z = 0.333$.

4 Fe(VI) in set 4(i) with $x = 0.416$ and $z = 0.147$.

2 Fe(VII) in set 2(d).

THE THORIUM-COBALT SYSTEM

Introduction

The thorium-cobalt system was initially studied by X-ray powder data alone. Binary alloys with compositions ranging from 0 to 100 atomic per cent cobalt were prepared and chemically analyzed for thorium and cobalt present. Five compounds with compositions roughly 33, 50, 70, 83, and 90 atomic per cent cobalt were found stable at room temperature.

The compound, Th_7Co_3, has been previously shown by Baenziger (2) to be isomorphous with Th_7Fe_3. A powder sample prepared from an alloy of approximately 83 atomic per cent cobalt indicated the presence of a compound, $ThCo_5$, isomorphous with $CaZn_5$. Single crystals of the three other compounds, ThCo, $ThCo_{2-3}$ and Th_2Co_{17}, were found in alloys corresponding roughly to their compositions. The compound, Th_2Co_{17}, was isomorphous with Th_2Fe_{17}. The only new structural types were those for ThCo and $ThCo_{2-3}$. However, there did appear to be some similarity between $ThFe_3$ and $ThCo_{2-3}$, though the compounds are obviously not isomorphous.

The usual difficulty of not having enough single crystals or a strictly one phase bulk alloy prevented direct chemical analyses or density determinations for these compounds. The compositions, therefore, are based upon the method of atomic volumes, powder data and the close relationship of this system to the thorium-iron system.

Structure of Th_7Co_3

The compound, Th_7Co_3, was found by Baenziger (2) to be isomorphous with Th_7Fe_3. It has an hexagonal unit cell with $\underline{a}_0$ = 9.83 Å and $\underline{c}_0$ = 6.17 Å. The atomic positions in space group C_{6v}^4 are the same as in Th_7Fe_3.

Structure of ThCo

Unit cell and space group

Powder data indicated a compound in the region of 50 atomic per cent cobalt 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, $\mu = 25°$, magnification factor = 6.00, and a voltage and current regulated General Electric XRD-3 unit using Mo Kα radiation (λ = 0.7107 Å). The crystal was found to be orthorhombic with $\underline{a}_0$ = 3.74 Å, $\underline{b}_0$ = 10.88 Å and $\underline{c}_0$ =4.16 Å.

The multiple film technique of Robertson (6) was used to obtain zero and first level Weissenberg diagrams for rotation about $\underline{c}_0$. Cu Kα radiation (λ = 1.5418 Å) and a camera of 5.73 centimeters diameter were employed.

Precession about $\underline{b}_0$ and $\underline{c}_0$ and rotation about $\underline{c}_0$ gave nets of C2ℓ symmetry in all levels. The Laue symmetry is, therefore, D_{2h}. The following extinctions were noted:

$(hk\ell)$ with $h + k = 2n + 1$.

$(h0\ell)$ with $h = 2n + 1$ and $\ell = 2n + 1$.

The only possible space groups are D_{2h}^{17} - Cmcm and C_{2v}^{12} - Cmc.

Composition of the phase

There were not enough single crystals to perform a chemical analysis or density determination. The composition of 50 atomic per cent cobalt was indicated by the powder data. The number of molecules per unit cell, four, is obtained by the method of atomic volumes, assuming a thorium atomic volume of 32.8 Å^3, a cobalt atomic volume of 11.1 Å^3, and a unit cell volume of 169.3 Å^3. Since only four-fold sets are allowed by the space groups, C_{2v}^{12} and D_{2h}^{17}, any other composition is highly improbable.

Atomic positions

The only atomic positions possible are the following:

C_{2v}^{12} - Cmc: (add 000;, 1/2 1/2 0)
4(a) 0yz; $0\bar{y}$ 1/2 + z.
D_{2h}^{17} - Cmcm: (add 000; 1/2 1/2 0)
4(a) 000; 00 1/2.
4(b) 0 1/2 0; 0 1/2 1/2.
4(c) 0y 1/4; $0\bar{y}$ 3/4.

Sets 4(a) and 4(b) of D_{2h}^{17} are not possible as the $\underline{c}_0$ axis, 4.16 Å, is too small to accomodate either two thorium (7.20 Å for coordination number 12) or two cobalt (5.00 Å for coordination number 12) atoms (13).

Since the number of parameters involved were few, at the most two y and two z parameters, a one-dimensional Patterson function, P(y), was plotted. See Figure 10. The major peak at $y = 1/4$, assumed to be a thorium-thorium interaction, indicated that the thorium y parameter was roughly 1/8 or 3/8. As both possibilities are equivalent in the allowed space groups, the value of 1/8 was selected. The signs of the structure factors for the (0k0) data were then determined and a one-dimensional electron density map, $\rho(y)$ was made. See Figure 11. The only peak to show up was the thorium atom at $y_{Th} = 0.132$. We can, without loss of generality, put $z_{Th} = 1/4$ since the only effect of the thorium z parameter is to shift the origin up the $\underline{c}_0$ axis.

In order to locate the cobalt atoms, a two-dimensional Patterson function, P(0y), was plotted. As there could be no x parameter in either C_{2v}^{12} or D_{2h}^{17}, only the section at $x = 0$ was calculated and subsequently plotted. See Figure 12. Two independent peaks appeared, one at $y = 0.272$ and the other at $y = 0.455$. The latter peak is no doubt due to a thorium-cobalt interaction. Knowing the thorium y parameter to be roughly 0.136, as indicated by P(0y), there

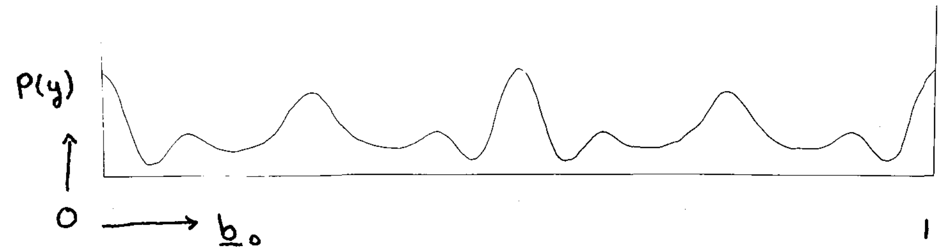

Figure 10. Patterson projection of ThCo onto $\underline{b}_0$ axis.

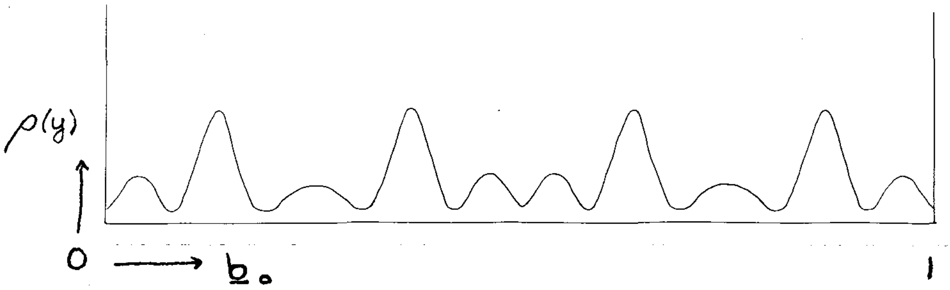

Figure 11. Electron-density projection of ThCo onto $\underline{b}_0$ axis.

are two ways of interpreting the peak at $y = 0.455$, either $y_{Co} = 0.318$ or $y_{Co} = 0.410$. The former is not possible as it would place the atoms too close together no matter what the value of z_{Co} may be. In order to obtain reasonable interatomic distances for the latter case, $y_{Co} = 0.410$, we must let $z_{Co} = 1/4$. As both z parameters are roughly 1/4, it appears that the crystal must belong to space group D_{2h}^{17}.

Refinement of parameters

Using the rough parameter values obtained from the Patterson function, P(Oy), $y_{Th} = 0.136$, and $y_{Co} = 0.410$, the signs of the structure factors for the (hk0) data were determined and a two-dimensional electron density plot, ρ(Oy), was made. See Figure 13. The values of the y parameters were found to be 0.136 for thorium and 0.418 for cobalt. A correction for non-termination of series error was made using calculated structure factors. The resulting atomic positions for ThCo in space group D_{2h}^{17} are:

4 Th at $0y\ 1/4$; $0\bar{y}\ 3/4$; $1/2\ 1/2 + y\ 1/4$;
$1/2\ 1/2 - y\ 3/4$ with $y = 0.136$.
4Co at same positions with $y = 0.416$.

The value of R, correlation factor, for the (hk0) and (hkl) data is 0.14. These data were corrected for absorption and temperature errors by methods similar to those applied to the Th_6Mn_{23} data. See Table X for a comparison

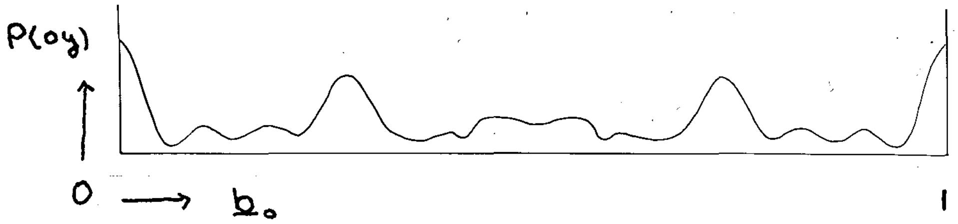

Figure 12. Section with x=0 of Patterson projection of ThCo onto (001).

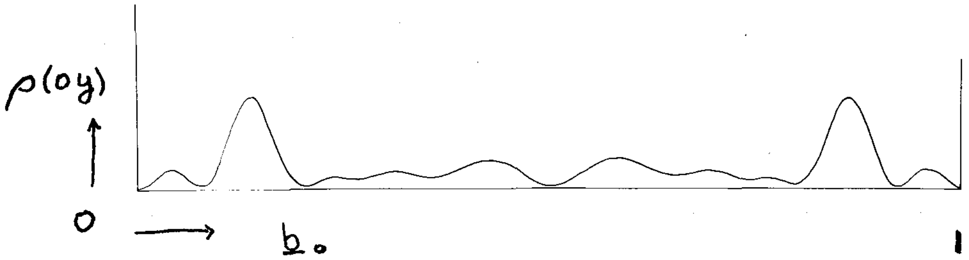

Figure 13. Section with x=0 of electron-density projection of ThCo onto (00).

of observed and calculated structure factors. A summary of interatomic distances is listed in Table XI. The arrangement of the atoms in the unit cell are shown in Figure 14.

Table X. Calculated and Observed Structure Factors for ThCo.

	$F_{calcd.}$	$F_{obsd.}$		$F_{calcd.}$	$F_{obsd.}$
(020)	+ 9	0	(021)	- 231	204
(040)	- 316	296	(041)	+ 144	190
(060)	+ 39	54	(061)	+ 234	233
(080)	+ 158	173	(081)	- 171	205
(0·10·0)	- 124	112	(0·10·1)	- 201	207
(0·12·0)	- 88	104	(0·12·1)	- 142	170
(110)	+ 127	166	(111)	- 264	186
(130)	- 254	205	(131)	- 230	177
(150)	- 59	54	(151)	+ 202	200
(170)	+ 289	225	(171)	+ 101	112
(190)	+ 51	26	(191)	- 157	187
(1·11·0)	- 228	230	(1·11·1)	- 16	20
			(1·13·1)	- 158	152
(200)	+ 339	278			
(220)	+ 2	0	(221)	- 195	168
(240)	- 265	222	(241)	+ 119	89
(260)	+ 36	30	(261)	- 207	163
(280)	+ 142	128	(281)	- 154	134
(2·10·0)	- 116	113	(2·10·1)	- 186	183
(2 12 0)	- 85	92	(2·12·1)	+ 134	144
(310)	+ 98	113	(311)	- 192	188
(330)	- 177	190	(331)	- 170	142
(350)	- 50	60	(351)	+ 162	133
(370)	+ 236	208	(371)	+ 83	75
(390)	+ 44	24	(391)	- 141	159
(400)	+ 242	212	(421)	- 150	177
(420)	- 1	16	(441)	+ 88	88
(440)	- 200	193	(461)	+ 165	162

Table XI. Interatomic Distances in ThCo.

Th	6 Th	3.62 Å
	2 Th	3.74 Å
	4 Co	2.86 Å
	3 Co	3.04 Å
Co	4 Th	2.86 Å
	3 Th	3.04 Å
	2 Co	2.77 Å

Structure of $ThCo_{2-3}$

Unit cell and space group

Single crystals of this compound were found in an alloy of approximately 67 atomic per cent cobalt. Single crystal data were obtained with a Buerger precession camera, $\mu = 25°$, and a magnification factor of 6.00. Both Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å) from a Philips diffraction unit and Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å) from a voltage and current regulated General Electric XRD-3 unit were used.

Using Mo $K\alpha$ radiation, the crystal appeared to be hexagonal with $\underline{a}_0 = 5.03$ Å and $\underline{c}_0 = 24.54$ Å. Precession about $\underline{c}_0$ gave nets of $C6\ell$ symmetry in all levels. The Laue symmetry is thus D_{6h}. The following systematic extinctions

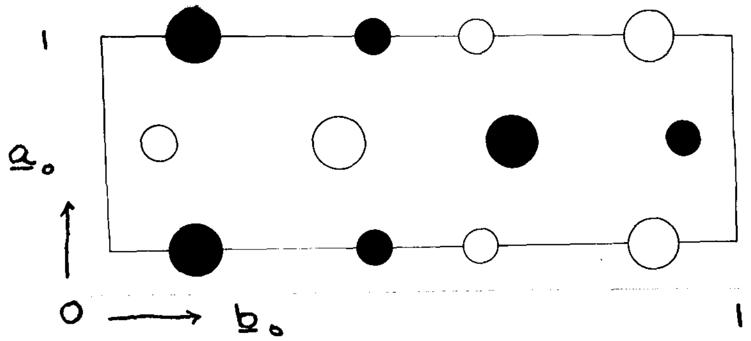

Figure 14. ThCo atomic positions projected onto (001) plane; thorium and cobalt atoms with z=1/4, corresponding large and small shaded circles; thorium and cobalt atoms with z=3/4, corresponding large and small unshaded circles.

were noted:

(HK·L) none.

(HK·0) except for H - K = 3n.

(HH·L) with L = 2n + 1.

The possible space groups are D_{6h}^{4} - C6/mmc, C_{6v}^{4} - C6mc, or D_{3h}^{4} - $C\bar{6}2c$.

However, as the higher (HH·L) layer line data were not well resolved, radiation of longer wave length Cu Kα, was then used. The reflections on the higher layer lines that appeared to be single reflections were now obviously several closely spaced spots. The spots, though distinguishable, were too close together to determine the exact multiplicity of the (00·L) data. The true $\underline{c}_0$ axis is roughly eight or nine times the previously chosen value of 24.54 Å. The structure thus appears to have a very large superlattice with a pseudo cell, $\underline{a}_0$ = 5.03 Å and $\underline{c}_0$ = 24.54 Å.

Composition of the phase

The powder data indicated a compound somewhere in the range 67 to 75 atomic per cent cobalt. As the true cell is very large, it is practically impossible to use the method of atomic volumes to get a better estimate of the composition of this phase. Not enough single crystals were available for chemical analysis or density determinations. One possible recourse is to make a thorough study of the thermal and microscopic properties of the alloys in this range of composition. This problem is being submitted for further study to the metallurgical section of the Ames Laboratory at Iowa State College.

Discussion

Some clue as to the possible arrangement of the atoms in the unit cell may be obtained from the systematic extinctions noted in the (HK·0) data, that is, those reflections missing except for H-K = 3n. These can be explained by placing atoms in positions with the x and y parameters having rhombohedral symmetry. This would require atoms of any one specie to be present in some multiple of three.

Taking a unit cell volume of 546.5 $\mathring{A}^3$, a thorium atomic volume of 32.8 $\mathring{A}^3$, and a cobalt atomic volume of 11.1 $\mathring{A}^3$, we find for

6 Th atoms,	31.5 Co atoms	(roughly $ThCo_5$),
9 Th atoms,	22.6 Co atoms	(roughly Th_2Co_5),
12 Th atoms,	13.8 Co atoms	(roughly ThCo).

The compositions corresponding to six and twelve thorium atoms per unit cell seem highly improbable as we have already identified phases corresponding to those compounds, ThCo and $ThCo_5$, which are completely different from this unknown phase. A phase having the composition, Th_2Co5, appears to be the only alternative. However, this formula composition is incompatible with the allowed space groups for the superlattice structure which all require an even number of atoms in the unit cell. It is thus not presently possible to ascertain what are the correct composition and structure for this phase.

Structure of $ThCo_5$

Powder diagrams, using a Debye-Scherrer camera and Cu Kα radiation (λ = 1.5418 Å), of an alloy containing approximately 83 per cent cobalt show this compound to be isomorphous to $CaZn_5$. The compound, $ThCo_5$, crystallizes in an hexagonal lattice with $\underline{a}_0$ = 5.01 Å and $\underline{c}_0$ = 3.97 Å. The atomic positions in space group D_{6h}^1 - C6/mmm are as follows:

1 Th at 000.
2 Co(I) at 1/3 2/3 0; 2/3 1/3 0.
3 Co(II) at 1/2 1/2 0; 1/2 0 1/2; 1/2 1/2 1/2.

A summary of interatomic distances is listed in Table XII.

Table XII. Interatomic Distances in $ThCo_5$

Th	6 Co	2.89 Å	Co(II)	4 Th	3.21 Å
	12 Co	3.21 Å		4 Co	2.51 Å
Co(I)	3 Th	2.89 Å		4 Co	2.46 Å
	6 Co	2.46 Å			

Structure of Th_2Co_{17}

This compound was found to be isomorphous with Th_2Fe_{17}. It has a monoclinic unit cell with $\underline{a}_0$ = 9.62 Å, $\underline{b}_0$ = 8.46 Å, $\underline{c}_0$ = 6.32 Å, and B = 99° 6'. The probable atomic positions in space group C_{2h}^3 - C2/m are the same as for Th_2Fe_{17}.

THE THORIUM-NICKEL SYSTEM

Introduction

The thorium-nickel system was initially studied by X-ray powder data alone. Binary alloys with compositions ranging from 50 to 96 atomic per cent nickel were prepared and chemically analyzed for thorium and nickel. Five compounds with compositions roughly 33, 50, 67, 83 and 90 atomic per cent nickel were found stable at room temperature. With the aid of single crystal data, the formulas representing these phases were ascertained to be Th_7Ni_3, ThNi, $ThNi_2$, $ThNi_5$ and Th_2Ni_{17}.

Prior to this X-ray study, there had been reported in the literature thermal and microscopic investigations of the thorium-nickel system by Horn and Basserman (20). Their results indicated the existence of five compounds, Th_2Ni, ThNi, Th_2Ni_5, $ThNi_5$ and $ThNi_9$. There thus appears to be fairly good agreement between the thermal and microscopic investigations and the X-ray studies. The discrepancies appear to lie within the limits of accuracy of the metallurgical data, but also may be partially due to vacancies occurring in the ideal lattice.

The structure of Th_7Ni_3 has been shown by Baenziger (2) to be isomorphous with Th_7Fe_3. The compound, $ThNi_5$, was found to be isomorphous with $CaZn_5$ and $ThNi_2$ crystallized with the well known AlB_2 type structure. The only new structural types were those for ThNi and Th_2Ni_{17}. However, there did appear to be some similarity between Th_2Ni_{17} and $ThNi_5$, and this will be discussed more fully in the final discussion section.

The Structure of Th_7Ni_3

The compound, Th_7Ni_3, was found by Baenziger (2) to be isomorphous with Th_7Fe_3. It has an hexagonal unit cell with $\underline{a}_0$ = 9.86 Å and $\underline{c}_0$ = 6.23 Å. The atomic positions in space group C_{6v}^4 are the same as in Th_7Fe_3.

The Structure of ThNi

Unit cell and space group

The powder data indicated a complex phase in the region of 50 atomic per cent nickel. Single crystals of this compound were obtained from an alloy containing approximately 40 atomic per cent nickel.

Single crystal data were obtained with a Buerger precession camera, μ = 25°, a magnification factor of 6.00, and a voltage and current regulated General Electric XRD-3 unit using Mo Kα radiation (λ = 0.7107 Å). The crystal was found to be orthorhombic with $\underline{a}_0$ = 14.15 ± .04 Å, $\underline{b}_0$ = 4.31 ± .02 Å and $\underline{c}_0$ = 5.73 ± .02 Å.

Precession about both $\underline{a}_o$ and $\underline{c}_o$ gave nets of $C2\ell$ symmetry in all levels. Inspection of the lattice constants indicates that the $\underline{b}_o$ axis cannot have symmetry greater than two-fold. If $\underline{b}_o$ had four-fold symmetry about itself, then $\underline{a}_o$ and $\underline{c}_o$ would have to be equal, and if $\underline{b}_o$ had either three or six-fold symmetry, then the ratio of the lattice constants, $\underline{a}_o$ to $\underline{c}_o$, would be 1 to 1.73. Therefore, the Laue symmetry is D_{2h}. The following systematic absences were noted:

$(hk\ell)$ none.

(hko) except for $h = 4n$.

$(ok\ell)$ with $k + \ell = 2n + 1$.

The space group is, consequently, either C_{2v}^{9} - Pn2a or D_{2h}^{16} - Pnma.

The following positions are possible in space groups C_{2v}^{9} and D_{2h}^{16}:

C_{2v}^{9} - Pn2a

4(a) xyz; $\bar{x}$ $1/2+y$ $\bar{z}$; $1/2-x$ $1/2+y$ $1/2+z$;
$1/2+x$ y $1/2-z$.

D_{2h}^{16} - Pnma

4(a) 000; 0 1/2 0; 1/2 0 1/2; 1/2 1/2 1/2.
(b) 00 1/2; 0 1/2 1/2; 1/2 00; 1/2 1/2 0.
(c) x $1/4$ z; $\bar{x}$ $3/4$ $\bar{z}$; $1/2-x$ $3/4$ $1/2+z$;
$1/2+x$ $1/4$ $1/2-z$.
8(d) xyz; $1/2+x$ $1/2-y$ $1/2-z$; $\bar{x}$ $1/2+y$ $\bar{z}$;

$1/2-x\ \bar{y}\ 1/2+z$; $\overline{xyz}$; $1/2-x\ 1/2+y\ 1/2+z$;
$x\ 1/2-y\ z$; $1/2+x\ y\ 1/2-z$.

Composition of the phase

The composition and the number of molecules per unit cell was based essentially upon the powder data, atomic volumes and space group considerations. Using a unit cell volume of $349.5\ \mathring{A}^3$, a thorium atomic volume of $32.7\ \mathring{A}^3$ and a nickel atomic volume of $10.9\ \mathring{A}^3$, the number of molecules of ThNi per unit cell was found to be eight. This is in agreement with the positions allowed by the space groups C_{2v}^{9} and D_{2h}^{16}, as one contains only four-fold atomic positions and the other both four and eight-fold sets. Any other possible composition, involving either four or twelve thorium atoms per unit cell, seems very unlikely as the unit cell is not large enough to accomodate twelve thorium atoms and with four thorium atoms the method of atomic volumes would lead to a composition $ThNi_5$.

Atomic positions

We can eliminate the space group, C_{2v}^{9}- Pn2a, by inspection of the Patterson function, P(xy). See Figure 15. All of the peaks of P(xy) lay on the lines $y = 0$ and $y = 1/2$, thus indicating that there are no appreciable general y parameters. The only values that y may have are 0 and 1/2 or 1/4 and 3/4. If y = 1/4 or 3/4, then the set 4(a) of C_{2v}^{9} is equivalent to 4(c) of D_{2h}^{16}. If we consider two four-fold sets in C_{2v}^{9} with both y values equal to zero or 1/2, this except for a shift in the origin of the unit cell, becomes equivalent to two sets of atoms in the 4(c) positions of space group D_{2h}^{16}. The only other possibility in C_{2v}^{9} is to have one four-fold set with y = 0 and another with y = 1/2. As the (hk0) data are absent except for h = 4n, we know that for every atom, at x_1, y_1, z_1, we must have an equivalent one, at 1/4 + z_1, y_2, z_2. Therefore, this last possibility would require on P(xy) a peak at (1/4 1/2) equivalent to that at (00). However, this equivalent peak occurs at (1/4 0) and we can thus eliminate space group C_{2v}^{9} - Pn2a from further consideration.

In space group D_{2h}^{16}, we can eliminate set 8(d). This involves a general y parameter which we have already shown to be either 0, 1/4, 1/2 or 3/4. For y equal to 1/4 or 3/4, this reduces to set 4(c) of the same space group. We cannot have y equal to either 0 or 1/2 as this would place the thorium or nickel atoms 2.16 Å apart. Using Pauling's radii (13) with coordination number twelve, this distance should be 3.60 Å for thorium and 2.50 Å for nickel. We can likewise eliminate sets 4(a) and 4(b) because of the very close interatomic distances. We therefore see that the eight thorium and eight nickel atoms must be placed in

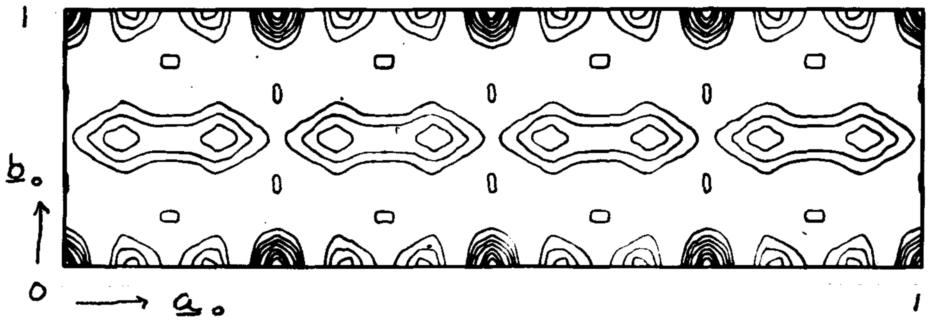

Figure 15. Patterson projection of ThNi onto (001).

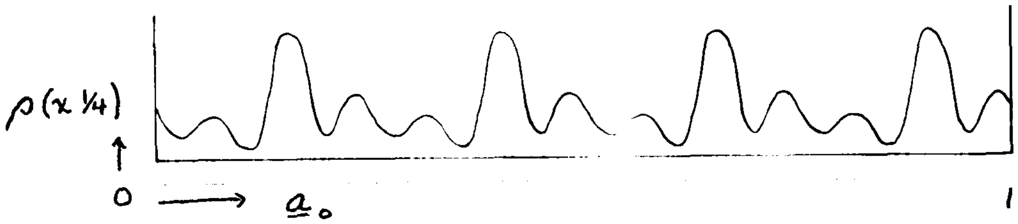

Figure 16. Section, with $y=1/4$, of electron-density projection of ThNi onto (001).

four four-fold sets of the type 4(c) in space group D_{2h}^{16}.

An inspection of the Patterson function, P(xy), suggests as possible parameters, $x_{Th(I)} = 5.4/60$, $x_{Th(II)} = 20.4/60$, $x_{Ni(III)} = 16.0/60$ and $x_{Ni(IV)} = 31.0/60$. A comparison of observed and calculated peak heights agrees very well and accounts for all observed peaks on the Patterson function, P(xy).

The Patterson function, P(yz), Figure 17, substantiates the fact that there are no general y parameters in the structure. There are only two independent peaks, one at (0 14/60) and the other at (0 1/2), not related by the symmetry of the space group. It thus appears that the z paremeters of the four sets must be multiples of approximately 1/8. If we assume both thorium sets to have the same z parameter, 8.0/60, we obtain reasonable thorium-thorium distances in the unit cell and also account for the peak at (0 14/60). We can also account for this peak, (0 14/60), by assuming that both thorium sets have the z parameter, 22/60, or that $z_I = 8/60$ and $z_{II} = 22/60$. However, we can eliminate both possibilities as the former only shifts the origin, whereas the latter would place thorium atoms too close together.

On the basis of P(yz) the possible z parameters for the nickel atoms are roughly 5/8 and 7/8. Investigation of interatomic distances shows that $z_{III} = 5/8$ and $z_{IV} = 7/8$

lead to reasonable distances.

Refinement of parameters

The approximate atomic positions obtained from the two-dimensional Patterson functions were used to determine the signs of the observed structure factors. Sections of two-dimensional electron density projections, ρ(xy) and ρ(yz), at y = 1/4 were plotted. See Figures 16 and 18. In order to correct for non-termination of series error, similar projections were made using calculated structure factors for only the observed reflections. As a result of this correction, the atoms were placed in the following positions in space group D_{2h}^{16} - Pnma:

4(c) x 1/4 z; $\bar{x}$ 3/4 $\bar{z}$; 1/2-x 3/4 1/2+z;
1/2+x 1/4 1/2-z.

4 Th(I) in set 4(c) with x = 0.094 and z = 0.140.
4 Th(II) in set 4(c) with x = 0.344 and z = 0.140.
4 Ni(III) in set 4(c) with x = 0.268 and z = 0.630.
4 Ni(IV) in set 4(c) with x = 0.518 and z = 0.870.

With these parameters, the correlation factor, R, for observed reflections was found to be 0.16. There did not appear to be any need for absorption or temperature corrections. The observed and calculated structure factors are given in Table XIII. The various distances between atoms are shown in Table XIV. The arrangement of the atoms in the unit cell is shown in Figure 19.

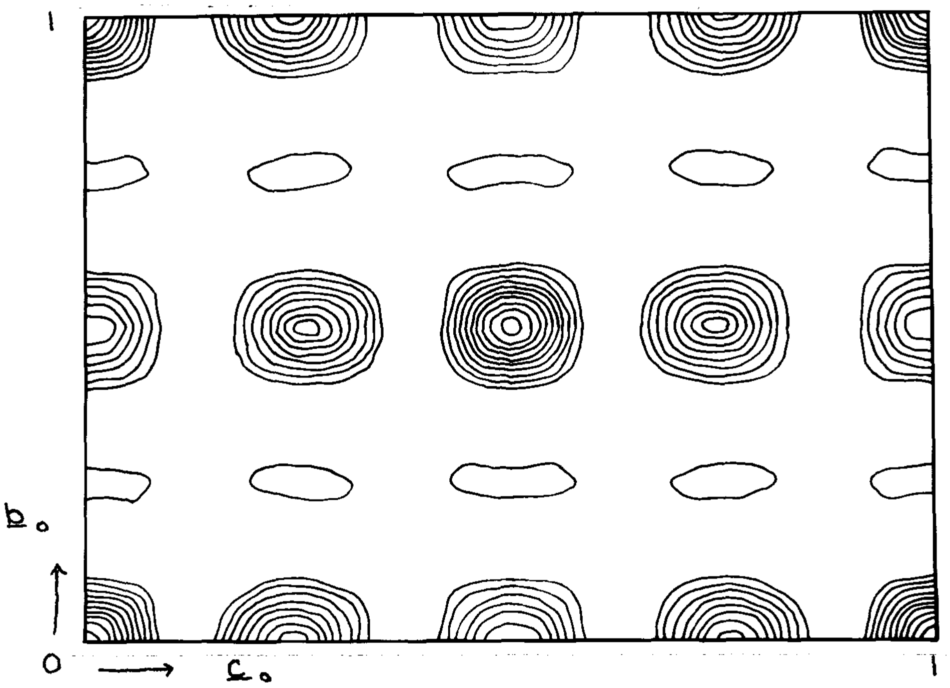

Figure 17. Patterson projection of ThNi onto (100).

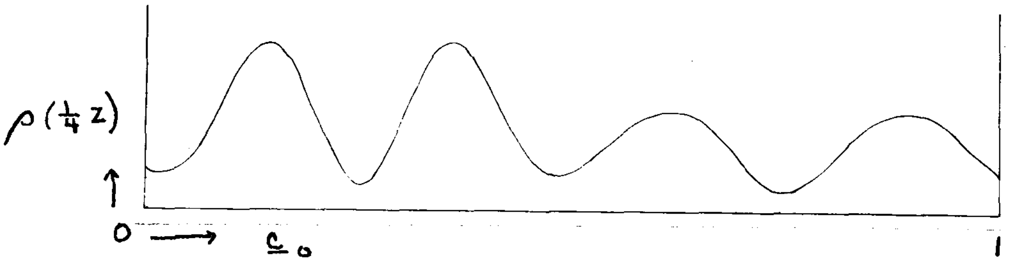

Figure 18. Section, with y=1/4, of electron-density projection of ThNi onto (100).

Table XIII. Calculated and Observed Structure Factors for ThNi

	$F_{\text{calcd.}}$	$F_{\text{obsd.}}$		$F_{\text{calcd.}}$	$F_{\text{obsd.}}$
(000)			(011)	- 343	213
(020)	- 720	746	(031)	+ 275	213
(040)	+ 520	581	(051)	- 225	244
(400)	- 274	270	(002)	- 124	0
(410)	- 492	424	(022)	+ 117	0
(420)	+ 245	159	(042)	- 82	0
(430)	+ 380	366			
(440)	- 200	74	(013)	- 160	0
			(033)	+ 138	0
(800)	+ 98	0	(053)	- 121	0
(810)	+ 401	445			
(830)	- 340	281	(004)	- 578	526
			(024)	+ 522	622
(12•0•0)	+ 326	466	(044	- 446	583
(12•1•0)	- 418	419			
(12•2•0)	- 304	419	(015)	+ 316	292
(12•3•0)	+ 364	376	(035)	- 293	318
(16•0•0)	- 401	445	(006)	+ 230	159
(16 1 0)	+ 292	223	(026)	- 186	184

Table XIV. Interatomic Distances in ThNi.

Th(I)	1 Th	3.54 Å	Ni(III)	2 Th	2.68 Å
	4 Th	3.70 Å		2 Th	2.91 Å
	2 Th	3.78 Å		1 Th	3.01 Å
	2 Th	3.79 Å		1 Th	3.11 Å
	1 Ni	3.01 Å	Ni(IV)	3 Th	2.91 Å
	1 Ni	3.11 Å		2 Th	2.98 Å
	2 Ni	2.91 Å		1 Th	3.01 Å
	2 Ni	2.98 Å		1 Th	3.11 Å
Th(II)	1 Th	3.54 Å		2 Ni	2.69 Å
	4 Th	3.70 Å			
	1 Th	3.79 Å			
	2 Ni	2.68 Å			
	3 Ni	2.91 Å			
	1 Ni	3.01 Å			
	1 Ni	3.11 Å			

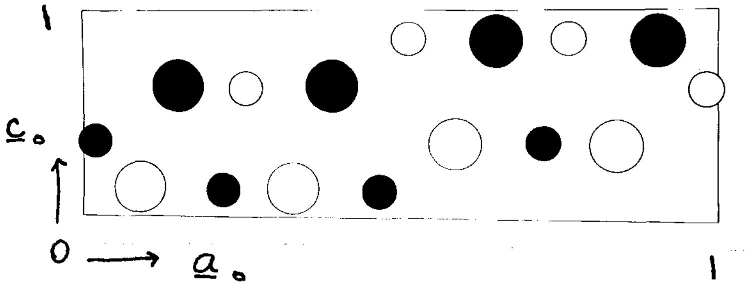

Figure 19. ThNi atomic positions projected onto (010) plane; thorium and nickel atoms with y=1/4, corresponding large and small unshaded circles; thorium and nickel atoms with y=3/4, corresponding large and small shaded circles.

The Structure of $ThNi_2$

The compound, $ThNi_2$, is hexagonal with $\underline{a}_0$ = 3.95 Å and $\underline{c}_0$ = 3.83 Å. The structure appears to be of the AlB_2 type with

1 Th at 000,
2 Ni at ±(1/3 2/3 1/2).

Multiple film powder data, using a Debye-Scherrer camera of radius 5.73 centimeters and CuKα (1.5418 Å) radiation, were obtained. Intensities calculated on the basis of this structure agree reasonably well with the observed powder data. See Table XV. A summary of interatomic distances is shown in Table XVI.

Table XV. Calculated and Observed Intensities for $ThNi_2$.

	$I_{calcd.}$	$I_{obsd.}$
(00·1)	9	3
(10·0)	65	55
(10·1)	199	100
(11·0)	79	50
(00·2)	22	14
(11·1)	8	25
(20·0)	10	25
(10·2)	18	25
(20·1)	46	50
(11·2)	44	50
(21.0)	8	20
(00·3)	6	20
(20·2)	8	
(21·1)	41	50
(10.3)	18	30
(30·0)	12	10
(30·1)	2	12
(11·3)	2	35
(21·2)	10	
(20·3)	12	12
(22·0)	9	5
(30·2)	18	12
(00·4)	3	7
(22·1)	2	
(31·0)	5	12
(10·4)	5	30
(31·1)	26	

Table XVI. Interatomic Distances in $ThNi_2$.

Th	12 Ni	2.99 Å
	6 Th	3.95 Å
	2 Th	3.83 Å
Ni	6 Th	2.99 Å
	3 Ni	2.29 Å

The Structure of $ThNi_5$

Unit cell and space group

The previous work by Rundle (3), using powder data alone, indicated a complex phase in the region 80-83 atomic per cent nickel. Single crystals of this compound were obtained from an alloy containing approximately 80 atomic per cent nickel. Single crystal data were obtained with a Buerger precession camera, $\mu = 30°$, a magnification factor equal to 5.50, and a Philips X-ray diffraction unit using Mo Kα radiation ($\lambda = 0.7107$ Å). The crystal was found to be hexagonal with $a_0 = 4.97$ Å and $c_0 = 4.01$ Å.

Precession about c_0 gave nets of C6 symmetry in all levels, indicating a D_{6h} Laue symmetry. There were no observed systematic extinctions. The possible space groups are D_{3h}^1 - $C\bar{6}m2$, C_{6v}^1 - C6mm, D_6^1 - C62, or D_{6h}^1 - C6/mmm.

Composition of the phase

The powder data indicated a range of composition $ThNi_{4-5}$. However, on the basis of atomic volumes the composition of this phase should be $ThNi_5$ and the number of molecules per unit cell should be one.

Atomic positions

On the bases of lattice constants and space group symmetry, it seemed highly probable that this compound, $ThNi_5$, was isomorphous with $CaZn_5$. Calculated intensities, see Table XVII, based on this structure compare reasonably well with the observed (HK·O) and (OO·L) data.

Table XVII. Calculated and Observed Intensities for $ThNi_5$.

	$I_{calcd.}$	$I_{obsd.}$		$I_{calcd.}$	$I_{obsd.}$
(10·0)	18	20	(41·0)	18	6
(11·0)	99	80	(50·0)	3	1
(20·0)	118	76	(33·0)	16	3
(21·0)	6	3	(42·0)	23	8
(30·0)	39	32	(51·0)	4	1
(22·0)	97	64	(00·1)	60	40
(31·0)	4	1	(00·2)	253	330
(40·0)	32	16	(00·3)	11	7
(32·0)	4	1	(00·4)	63	40

The atomic positions are as follows:

1 Th at 000.

2 Ni(I) at 1/3 2/3 0; 2/3 1/3 0.

3 Ni(II) at 0 1/2 1/2; 1/2 0 1/2; 1/2 1/2 1/2.

A summary of interatomic distances are listed in Table XVIII.

Table XVIII. Interatomic Distances in $ThNi_5$

Th	6 Ni	2.87 Å
	12 Ni	3.20 Å
Ni(I)	3 Th	2.87 Å
	6 Ni	2.47 Å
Ni(II)	4 Th	3.20 Å
	4 Ni	2.49 Å
	4 Ni	2.47 Å

The Structure of Th_2Ni_{17}

Unit cell and space group

The powder data indicated a complex phase related to the $ThNi_5$ structure in the region of 90 to 92 atomic per cent nickel. Single crystals of this compound were obtained from an alloy containing approximately 90 atomic per cent nickel.

Single crystal data were obtained with a Buerger precession camera, $\mu = 25°$, a magnification factor of 6.00 and a voltage and current regulated General Electric XRD-3 unit using Mo Kα radiation ($\lambda = 0.7107$ Å). Weissenberg data were also obtained with a Philips X-ray diffraction unit using Cu Kα radiation ($\lambda = 1.5418$ Å). The crystal was found to be hexagonal with $\underline{a}_0 = 8.37$ Å and $\underline{c}_0 = 8.14$ Å.

Precession about $\underline{c}_0$ gave nets of $C6\ell$ symmetry in all levels, indicating a D_{6h} Laue symmetry. The following systematic absences were noted:

(HK·L) none.
(HO·L) none.
(HH·L) with $L = 2n + 1$.

The allowed space groups are therefore D_{6h}^{4} - $C6/mmc$, C_{6v}^{4} - $C_{6}mc$, and D_{3h}^{4} - $C\bar{6}2C$.

Composition of the phase

There were not enough single crystals to perform a direct chemical analysis or a density determination. Therefore, the composition and the number of molecules per unit cell were essentially based upon atomic volumes and space group considerations.

With the above allowed space groups, it is only possible to have an even number of molecules per unit cell. Using a unit cell volume of 494.2 Å^3, a thorium atomic volume of 32.7 $\mathring{A}^3$ and a nickel atomic volume of 10.9 $\mathring{A}^3$, we find for

2 Th atoms, 39.3 Ni atoms (roughly $ThNi_{20}$)
4 Th atoms, 33.3 Ni atoms (roughly $ThNi_{8.5}$)
6 Th atoms, 27.3 Ni atoms (roughly $ThNi_{4.5}$).

Since the compositions corresponding to two and six thorium atoms per unit cell is highly improbable, it was assumed that the composition of this phase is in the range of $ThNi_{8-9}$.

Postulated structure

No intensity data were obtained for this phase so that it was not possible, by Patterson and electron density projections, to determine the atomic positions directly. However, the powder and single crystal data show such a close relationship to that of $ThNi_5$ that it is possible to postulate a most probable structure for Th_2Ni_{17}. This can be done by selecting $\underline{a}_0(Th_2Ni_{17}) \approx \sqrt{3}\underline{a}_0'(ThNi_5)$ and $\underline{c}_0(Th_2Ni_{17}) \approx 2\underline{c}_0'(ThNi_5)$. This new unit cell comprises approximately six of the $ThNi_5$ unit cells and without any substitution of thorium atoms by nickel atoms would have the formula Th_6Ni_{30}.

As we know that there are four thorium atoms per unit cell we must replace two of the six thorium atoms by nickel atoms. Since the atomic volume of thorium is roughly three times that of nickel, we might expect the thorium atoms to be replaced by six nickel atoms and so obtain the formula $ThNi_9$. However, on the basis of packing considerations, it would be impossible to place three nickel atoms in the hole left vacant by the removal of thorium. In addition, there is a small shrinkage in the lattice constant, $\underline{a}_0$ $(Th_2Ni_{17}) = 8.37$ Å compared to the expected value $\sqrt{3}\, \underline{a}_0'(ThNi_5) = 8.60$ Å. Finally, the previous calculations using the method of atomic volumes indicate 34 nickel atoms per unit cell so that the composition appears to be Th_2Ni_{17} and not $ThNi_9$.

In order to maintain the symmetry indicated by the allowed space groups, D_{6h}^4 - C6/mmc, C_{6v}^4 - C6mc and D_{3h}^4 - $C\bar{6}2c$, we must remove either the two thorium atoms along the $\underline{c}_0$ axis or two of the atoms in the four-fold positions. The former is unlikely as it would require four nickel atoms to be placed along the $\underline{c}_0$ axis. This axis is too short, 8.14 Å, in comparison to the expected value of 9.96 Å obtained by using Pauling's (13) values for metallic radii. If we remove two thorium atoms from the general four-fold set, then we must place the remaining two in a special two-fold set. This leads to the following approximate positions for the atoms of Th_2Ni_{17} in space group D_{6h}^4 - C6/mmc with two molecules per unit cell.

2 Th(I) at 00 1/4; 00 3/4.

2 Th(II)	at 1/3 2/3 3/4; 2/3 1/3 1/4.
6 Ni(i)	at 1/2 00; 0 1/2 0; 1/2 1/2 0; 1/2 0 1/2; 0 1/2 1/2; 1/2 1/2 1/2.
12 Ni(II)	at x0 1/4; 0x 1/4; xx 1/4; $\bar{x}$o 1/4; 0$\bar{x}$ 1/4; $\overline{xx}$ 1/4; x0 3/4; 0x 3/4; xx 3/4; $\bar{x}$0 3/4; 0$\bar{x}$ 3/4; $\overline{xx}$ 3/4 with $x = 1/3$.
12 Ni(III)	at x 2x 0; $\overline{2x}$ $\bar{x}$ 0; x$\bar{x}$0; x $\overline{2x}$ 0; 2x x 0; $\bar{x}$ x 0; x 2x 1/2; $\overline{2x}$ $\bar{x}$ 1/2; x $\bar{x}$ 1/2; $\bar{x}$ $\overline{2x}$ 1/2; 2x x 1/2; $\bar{x}$ x 1/2 with $x = 1/6$.
4 Ni(IV)	at 1/3 2/3 z; 2/3 1/3 z; 2/3 1/3 1/2+z; 1/3 2/3 1/2-z with $z = 0.11$.

DISCUSSION

Introduction

The composition of intermetallic compounds bears in general little relation to the customary valences of the metals. The significant factors, which at present are only partially understood, are the ratio of valence electrons to atomic nuclei, relative values of metallic radii and differences in electronegativity of combining atoms.

The compounds of thorium with the transition elements of the first period are particularly numerous and interesting and display several new structural types. Attempts to correlate these intermetallic compounds with one another and with intermetallic compounds in general will be based essentially upon empirical considerations. The two factors to be considered are the relative values of metallic radii and the electron to atom ratio.

As one of the characteristic properties of metal structures is a close packing of atoms, it is evident that differences in the sizes of combining atoms will lead to different atomic arrangements and hence to different crystal structures. However, many structures which appear to be unrelated, that is, have different atomic ratios or belong to different crystal classes, show many similarities upon inspection of the packing polyhedra within the unit cell. It would thus appear to be promising to study the nature of these polyhedra and the conditions that lead to their stability in crystal structures.

Since metals that have approximately the same radius ratio do not all form similar compounds, electronic or electronegativity effects must also be of importance for compound formation. Many intermetallic compounds, electron compounds, with closely related structure but different chemical composition have the same electron to atom ratios. The stability of some of these compounds has been explained on the basis of zone theory (21, 22) and is shown to be dependent upon the electron to atom ratio.

Stability of the Laves phases

Many intermetallic compounds with the formula AB_2 are found to have a structure isomorphous with one of the three Laves phases (23), the hexagonal $MgZn_2$ phase, the cubic $MgCu_2$ phase or the more complex hexagonal $MgNi_2$ phase. The common feature of these three structures is that they are formed by various systematic packings of the same polyhedron, Figure 1, which consists of a large atom, A, surrounded by twelve smaller B atoms at the corners of a truncated tetrahedron with all the edges of equal length. The various ways in which polyhedra of this form pack in three-dimensional space lead to the three different structures.

The stability of these phases appears to be partially dependent upon the radius ratio of the A to B atoms. Though the ideal ratio is 1.25, compounds with the ratio of 1.12 to 1.50 are known. Many compounds of this type are formed by titanium and zirconium with the transition elements, whereas only manganese forms a Laves type compound with thorium. As the valence of titanium, zirconium and thorium is the same, by considering the Laves phases formed by these elements we can study the size effect of the A atom on the stability of the compounds without having to pay special attention to any electronic effects. The distances observed and calculated on the basis of Pauling's radii (13) are listed in Table XIX.

By fixing one interatomic distance in the unit cell, we in turn fix all of them. The observed and calculated A-B distances seem in general to agree quite well. This suggests that it is the A-B distance which determines the size of the polyhedron and hence of the unit cell. As we go from transition elements of high atomic number to those of lower atomic number we find poor agreement with observed and calculated A-B distances at that element beyond which this phase is no longer formed. The stability of the phase thus appears to be connected in some as yet unknown way with the A-B distance.

Table XIX. Interatomic Distances in Laves Phases.

		Observed Distance	Calculated Distance
$TiMn_2$:	Ti - Ti	2.95 Å	2.97 Å
	Ti - Mn	2.82	2.81
	Mn - Mn	2.41	2.61
$TiFe_2$:	Ti - Ti	2.92	2.97
	Ti - Fe	2.79	2.79
	Fe - Fe	2.38	2.52
$TiCo_2$:	Ti - Ti	2.90	2.97
	Ti - Co	2.78	2.76
	Co - Co	2.37	2.50
ZrV_2:	Zr - Zr	3.24	3.20
	Zr - V	3.10	2.98
	V - V	2.65	2.68
$ZrCr_2$:	Zr - Zr	3.14	3.23
	Zr - Cr	3.00	2.99
	Cr - Cr	2.56	2.71
$ZrMn_2$:	Zr - Zr	3.08	3.23
	Zr - Mn	2.95	2.94
	Mn - Mn	2.51	2.61
$ZrFe_2$:	Zr - Zr	3.05	3.23
	Zr - Fe	2.92	2.92
	Fe - Fe	2.49	2.52
$ZrCo_2$:	Zr - Zr	2.98	3.23
	Zr - Co	2.85	2.89
	Co - Co	2.43	2.50
$ThMn_2$:	Th - Th	3.35	3.63
	Th - Mn	3.21	3.14
	Mn - Mn	2.74	2.61

Relation between $ThMn_{12}$, Th_2Fe_{17}, Th_2Co_{17}, Th_2Ni_{17} and the $MgZn_5$ lattice

The compounds with high transition element composition, $ThMn_{12}$, Th_2Fe_{17}, Th_2Co_{17} and Th_2Ni_{17}, are all related even though the compounds belong to different crystal classes. The structures are based on the $MgZn_5$ lattice in which thorium now replaces magnesium and the transition element replaces zinc. By systematically replacing particular thorium atoms in the $MgZn_5$ lattice with pairs of transition element, the superlattices of hexagonal Th_2Ni_{17}, monoclinic Th_2Fe_{17} and Th_2Co_{17}, and body-centered tetragonal $ThMn_{12}$ can be derived.

The projection of the atoms along the $\underline{c}_0$ axis onto the (001) plane of the $MgZn_5$ lattice is shown in Figure 20. In order to obtain the superlattice of the compounds with high transition element content we replace the following thorium atoms by pairs of the corresponding transition element parallel to the $\underline{c}_0$ axis of the $MgZn_5$ lattice:

$ThMn_{12}$: first layer, B_1, B_2, B_3,..., D_1, D_2....
second layer, A_1, A_2, A_3,..., C_1, C_2,...

Th_2Fe_{17} and Th_2Co_{17}:
first layer, B_2, B_5,..., D_2, D_5,....
second layer, B_3, B_6,..., D_3, D_6,....
third layer, A_3, A_6,..., C_3, C_6,....

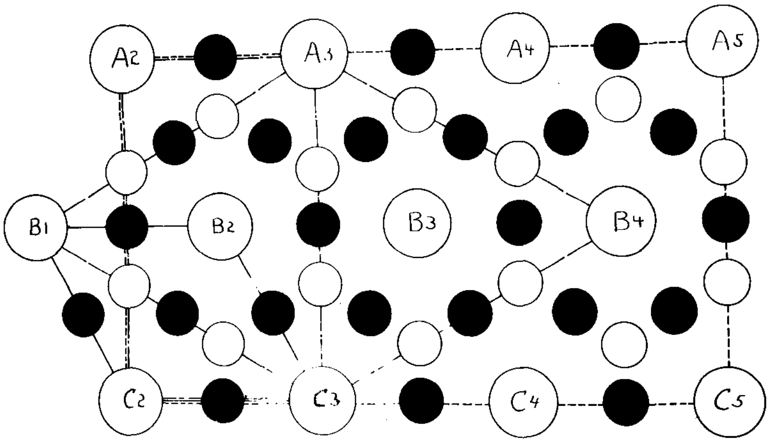

Figure 20. Projection of $MgZn_5$ type lattice onto (001) plane; thorium atoms, large circles; transition element atoms with $z=0$, small unshaded circles; transition element atoms with $z=1/2$, small shaded circles; $MgZn_5$ type unit cell, solid line; $ThMn_{12}$ unit cell, dash-dot line; Th_2Fe_{17} or Th_2Co_{17} unit cell, short dashes; Th_2Ni_{17} unit cell, long dashes.

Th_2Ni_{17}: first layer, B_2, B_5,...., D_2, D_5,....
second layer, B_3, B_6,...., D_3, D_6,....

Though it is interesting to note the similarities between these structures, the reasons for the different methods of substitution are still not understood.

Electron compounds and the thorium-manganese system

It has been pointed out by Hume-Rothery (24) that certain intermetallic compounds, electron compounds, with closely related structures but different chemical composition can be considered to have the same electron to atom ratio. There are three general types of electron compounds, β, γ, and ϵ phases corresponding to the electron to atom ratios of 1.5, 1.615 and 1.75. The valences generally assumed by Hume-Rothery for some of the elements forming these compounds are listed in Table XX.

Some question as to the correctness of these metallic valences of the transition elements has been raised by Pauling (13, 25, 26). In Pauling's treatment of the metallic state, the five d-orbitals are partitioned into 2.44 non-binding or atomic d-orbitals while the remaining 2.56 d-orbitals hybridize with the one s and three p orbitals to give 5.78 orbitals used for bonding and 0.78 unused, or 'metallic', orbitals which are regarded as characteristic of the metallic state.

Table XX. Metallic Valences of Some Metals Which Form Electron Compounds

	Hume-Rothery	Pauling
Cu	1	5.44
Zn	2	4.44
Ga	3	3.44
Ni	0	5.78
Co	0	5.78
Fe	0	5.78
Mn		4.16 5.78
Th	4	4
Al	3	3

Using Pauling's values (13) of metallic valences, listed in Table XX, one finds the electron to atom ratios of 4.94, 4.82 and 4.69 for the β, γ and ϵ phase. However, it can be shown (27) that constant electron to atom ratios for elements forming these phases result if the valences change in an arithmetical progression as one goes across the periodic table.

In most of the previously reported electron compounds, either Pauling's or Hume-Rothery's valences will give consistent electron to atom ratios. It appears that the three compounds $ThMn_{12}$, Th_6Mn_{23} and $ThMn_2$ might be related to the β, γ and ϵ phases. The β phase is body-centered cubic whereas $ThMn_{12}$ is body-centered tetragonal; the γ phase and

Th_6Mn_{23} are complex face-centered cubic structures; and both the ε phase and $ThMn_2$ form close-packed hexagonal structures. Both Pauling and Hume-Rothery agree on the thorium valence being four so that by assuming the three intermetallic compounds to be electron compounds it is possible to calculate the manganese valence for each. The values obtained are listed in Table XXI.

Table XXI. Manganese Valences in $ThMn_2$, Th_6Mn_{23} and $ThMn_{12}$.

	Using Hume-Rothery's Ratios	Using Pauling's Ratios
$ThMn_2$	.63	5.02
Th_6Mn_{23}	.99	5.04
$ThMn_{12}$	1.29	5.04

It is thus apparent that only the Pauling valences give consistent results. The valence of five is in good agreement with the average value of the two valences, 4.16 and 5.78, given to manganese by Pauling (13).

Possible electron compounds in the thorium-iron, thorium-cobalt and thorium nickel systems

The fact that the four compounds, $ThMn_{12}$, Th_2Fe_{17}, Th_2Co_{17} and Th_2Ni_{17}, are related makes one suspect that they may be electron compounds corresponding to the β phase of Hume-Rothery. The valences given by Pauling to iron, cobalt and nickel are the same and somewhat higher than for manganese so it might be expected that the compounds, Th_2Fe_{17}, Th_2Co_{17} and Th_2Ni_{17}, would contain a lower concentration of transition element than the corresponding manganese compound, $ThMn_{12}$.

The phases, Th_7Fe_3, Th_7Co_3 and Th_7Ni_3, are hexagonal and it might be supposed that these compounds correspond to the ε phase of Hume-Rothery. Similarly, ThNi and ThCo are complex phases and these may be supposed to correspond to the γ phase of Hume-Rothery. As there is no ThFe compound stable at room temperature, it would appear to be very interesting to study the thorium-iron system at higher temperatures in order to detect the possible existence of this compound. These electron compounds may have a fairly wide composition range of stability such that the β phase extends, for the thorium-iron system, from $ThFe_3$ through $ThFe_5$ to Th_2Fe_{17}, for the thorium cobalt system, from $ThCo_{2-3}$ through $ThCo_5$ to Th_2Co_{17}, and for the thorium-nickel system, from $ThNi_2$ through $ThNi_5$ to Th_2Ni_{17}. This does not appear to be too unreasonable as the 1-5 and 2-17 compounds are known to be related. As there is still some question as to the nature of the $ThFe_3$ and $ThCo_{2-3}$ phases, there may be some overlapping between the β and γ phases.

The transition metals, manganese through cobalt, fluoresce in copper radiation, while nickel does not. It was only in the thorium-nickel system that it was possible to study by powder diffraction methods the mechanism of the substitution of thorium by transition metal atoms in the range ThM_5 - Th_2M_{17}. Alloys of intermediate nickel composition gave powder diagrams indicating a continuous shrinkage of the $\underline{a}_0$ lattice constant. This is in agreement with and tends to confirm the assumption that the β phase for the thorium-iron, thorium-cobalt and thorium-nickel systems has a wide composition range of stability.

SUMMARY

The binary alloy systems of thorium with manganese, iron, cobalt and nickel have been investigated by X-ray diffraction methods for the presence of room temperature stable intermetallic compounds. It has been found that thorium forms three compounds with manganese, $ThMn_2$, Th_6Mn_{23} and $ThMn_{12}$, four with iron, Th_7Fe_3, $ThFe_3$, $ThFe_5$ and Th_2Fe_{17}, five with cobalt, Th_7Co_3, ThCo, $ThCo_{2-3}$, $ThCo_5$ and Th_2Co_{17}, and five with nickel, Th_7Ni_3, ThNi, $ThNi_2$, $ThNi_5$ and Th_2Ni_{17}.

The structures, $ThMn_2$, Th_6Mn_{23}, $ThMn_{12}$, Th_7Fe_3, Th_7Co_3, ThCo, $ThCo_5$, Th_7Ni_3, ThNi, $ThNi_2$, $ThNi_5$, have been completely determined. Though not completely verified the structures, $ThFe_5$, Th_2Fe_{17}, Th_2Co_{17} and Th_2Ni_{17}, are fairly well established. The structures of $ThFe_3$ and $ThCo_{2-3}$ are still unknown.

The compounds, Th_6Mn_{23}, $ThMn_{12}$, Th_7Fe_3, Th_2Fe_{17}, ThCo, ThNi and Th_2Ni_{17}, represent new structural types. The compounds, Th_7Co_3 and Th_7Ni_3, are isomorphous with Th_7Fe_3, Th_2Co_{17} with Th_2Fe_{17}, and $ThFe_5$ and $ThCo_5$ with $ThNi_5$.

The composition of these intermetallic compounds bears little relation to the customary valences of the metals. Attempts to correlate these compounds with one another and with intermetallic compounds in general has been based essentially upon a consideration of the relative values of of metallic radii, which dependent upon the sizes of the combining atoms will lead to different atomic arrangements, and of the ratio of valence electrons to atomic nuclei.

A study of the Laves phases, common to many compounds with the formula AB_2 and a radius ratio of approximately 1.25, suggests that it is the A-B distance which determines the size of the polyhedra comprising the unit cell. Inspection of the lattices and coordination polyhedra of the compounds, $ThMn_{12}$, Th_2Fe_{17}, Th_2Co_{17}, Th_2Ni_{17} and $ThNi_5$, shows that they are related to one another though the compounds belong to different crystal classes.

It appears that the compounds, $ThMn_{12}$, Th_6Mn_{23} and $ThMn_2$, are related to the electron compounds, β, γ and ϵ phases, with electron to atom ratios of 1.5, 1.615 and 1.75 on the basis of Hume-Rothery's valences or with the ratios of 4.94, 4.82 and 4.69 on the basis of Pauling's valences. However, only Pauling's ratios give a consistent value for the valence of manganese. It also appears probable that the compounds in the thorium-iron, thorium-cobalt and thorium-nickel systems are electron compounds.

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