accuracy of the $x$ coordinates makes it impossible to quote accurate bond lengths and angles. The values calculated from the coordinates given in Table 1 are
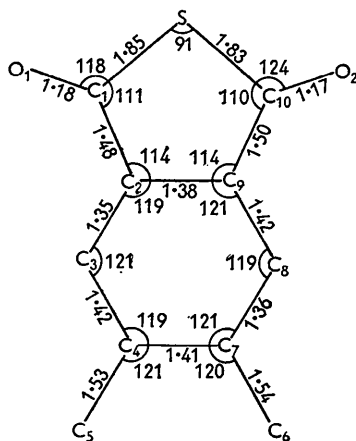


Fig. 3. Bond lengths, in Ångström units.
Valence angles in degrees.

shown in Fig. 3. The intermolecular distances are nowhere less than 3·5 Å and are attributable to van der Waals forces. Fig. 2 shows quite clearly the positions of the two hydrogen atoms attached directly to the benzene ring, and there is markedly high electron density in the vicinity of the carbonyl bonds. The significance of the latter detail is, however, doubtful, as the standard deviation for the electron density in this projection is 0·3 e.Å$^{-2}$ and the Fourier synthesis is subject to termination-of-series errors.

I am indebted to Prof. A. J. C. Wilson for guidance and for the use of apparatus purchased with a Royal Society grant, and to Mr G. Burrows for suggesting the problem and supplying the specimens.

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# Compounds of Thorium with Transition Metals. II. Systems with Iron, Cobalt and Nickel*

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The compositions of the compounds of thorium with iron, cobalt, nickel and copper have been summarized in a previous paper. Details of the structures of these compounds, together with a brief description of the structure determinations of the new structural types, are given here. Certain relationships among the compounds are noted.

## Methods

Studies of powder diagrams of the Th–$M$ systems were made to determine the number and approximate compositions of the compounds stable (or metastable) at room temperature. Single crystals were subsequently found for almost all the observed phases. This was usually most easily accomplished for two-phase material, and seldom was enough strictly one-phase material obtainable to settle compositions precisely by chemical means. Final compositions were decided

by approximate chemical compositions, coupled with atomic volume and space-group considerations, and finally, in most cases, by complete structure determinations. The thermal and microscopic study of the Th–Ni system by Horn & Basserman (1948) is in reasonable agreement with our results.

Except for the Th$_7M_3$ compounds, described below, data were collected with Weissenberg cameras and copper radiation or precession cameras and molybdenum radiation. Intensities were estimated visually using multiple films for copper radiation and timed exposures for molybdenum. In the latter case a G. E. XRD-3 diffraction unit with current and voltage stabilization was used as an X-ray source.

Absorption was inevitably a complicating factor in these studies, especially since crystal fragments isolated from alloys often had peculiar shapes and were

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not of ideal size. Absorption corrections were often very rough, and sometimes omitted.

Structure determinations usually proceeded by means of two-dimensional Patterson and Fourier syntheses, using IBM equipment in the calculations. Most of these were straightforward, and only outlines of the methods are indicated below. In all cases where a structure was obtained it was refined by two-dimensional Fourier methods, including synthetic Fouriers unless otherwise noted. Final electron-density projections will be given in this paper.

## The $Th_7M_3$ compounds

Isomorphous hexagonal iron, cobalt and nickel compounds of high thorium content were found in these systems, and brittle, hexagonal needles of all three compounds were obtained. Material of nearly one phase gave a chemical analysis of $\sim 28$ atomic% transition metal. Lattice constants of the three compounds are:

|        | $Th_7Fe_3$ | $Th_7Co_3$ | $Th_7Ni_3$ |
|--------|------------|------------|------------|
| $a$ (Å) | 9·85       | 9·83       | 9·86       |
| $c$ (Å) | 6·15       | 6·17       | 6·23       |

Unit-cell volumes are $\sim 520$ Å$^3$, and the atomic volume of Th is 32·9 Å$^3$, while atomic volumes of the transition metals are about 11 Å$^3$. These volumes, together with the approximate composition, lead to a unit-cell content of $Th_{14}M_{5-6}$. Only $Th_{14}M_6$ is compatible with the final structure.

The Laue symmetry, as determined from oscillation photographs, was $D_{6h}$ for all three compounds, with only one systematic extinction, $(HH.L)$ with $L = 2n+1$. Because of the low scattering power of the transition metals we considered this extinction binding only on thorium. The cell dimensions, however, eliminate putting two thoriums above each other along $c$, or twelve thorium atoms in one hexagonal plane. A Patterson projection, $P(x, y)$, for $Th_7Fe_3$



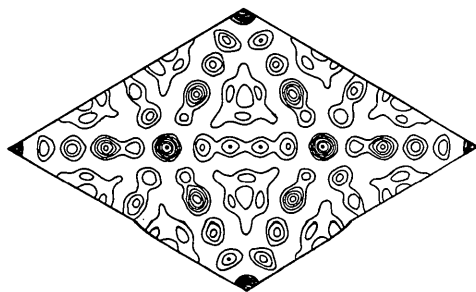Fig. 1. Patterson projection of $Th_7M_3$ on to (0001).

(Fig. 1) clearly indicated positions for thorium as follows:

2 Th$_1$ at $\pm[\frac{1}{3}, \frac{2}{3}]$;
6 Th$_2$ at $\pm[x, 2x; 2x, x; x, \bar{x}]$, with $x_2 = 0·122$;
6 Th$_3$ at $\pm[x, 2x; 2x, x; x, \bar{x}]$, with $x_3 = 0·544$.

The holes in the structure correspond to the same set of sixfold positions with $x_4 = 0·833$, and placing iron atoms in these holes was consistent with minor peaks on the Patterson projection.

Signs of $F_{hk0}$ were obtained from the above structure, and $\varrho(x, y)$ was calculated, yielding the more reliable parameters

$$x_2 = 0·126, \quad x_3 = 0·539, \quad x_4 = 0·800.$$

General reflections, $(HK.L)$, clearly require $z$ parameters, and of the choices of space groups only $C_{6v}^4$–$C6mc$ is satisfactory spatially. Absorption factors became so important in determining $z$ parameters that these parameters were determined only roughly for thorium, and packing considerations had to be used to settle the $z$ parameter for iron.

The final structure, based on $C6mc$, is:

2 Th$_1$ at 2$(b)$: $(\frac{1}{3}, \frac{2}{3}, z)$; $(\frac{2}{3}, \frac{1}{3}, \frac{1}{2}+z)$, with $z_1 = 0·06$;

6 Th$_2$ at 6$(c)$: $(x, 2x, z)$; $(\overline{2x}, \bar{x}, z)$; $(x, \bar{x}, z)$; $(\bar{x}, \overline{2x}, \frac{1}{2}+z)$; $(2x, x, \frac{1}{2}+z)$; $(x, x, \frac{1}{2}+z)$, with $x_2 = 0·126$, $z_2 = 0·250$;

6 Th$_3$ in 6$(c)$, with $x_3 = 0·544$, $z_3 = 0·03$;

6 $M_4$ in 6$(c)$, with $x_4 = 0·815$, $z_4 = 0·31$.
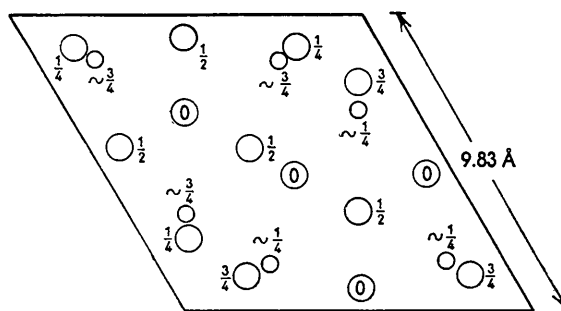
A projection of the structure on to (001) is shown



Fig. 2. The projection of the $Th_7M_3$ structure on to (0001) (for the true $z$ coordinates see text).

in Fig. 2 in which the rounded-off $z$ parameters are given. Interatomic distances are given in Table 1.

Table 1. *Interatomic distances in* $Th_7Fe_3$

| Th$_I$ | 2 Fe | 2·89 Å | Th$_{III}$ | 3 Fe | 2·96 Å |
|--------|------|--------|------------|------|--------|
|        | 2 Fe | 2·90 |        | 3 Th$_{II}$ | 3·60 |
|        | 2 Th$_{III}$ | 3·55 |        | 3 Th$_{II}$ | 3·70 |
|        | 2 Th$_I$ | 3·72 | Fe | 2 Th$_I$ | 2·89 |
|        | 4 Th$_I$ | 3·80 |        | 1 Th$_I$ | 2·90 |
| Th$_{II}$ | 2 Fe | 2·91 |        | 2 Th$_{II}$ | 2·91 |
|        | 2 Th$_{III}$ | 3·43 |        | 1 Th$_{III}$ | 2·96 |
|        | 2 Th$_I$ | 3·55 |        |      |      |
|        | 1 Th$_{III}$ | 3·60 |        |      |      |
|        | 1 Th$_{III}$ | 3·70 |        |      |      |
|        | 2 Th$_{II}$ | 3·76 |        |      |      |

This structure was determined during the war before good single-crystal cameras were available in this Laboratory and during a time when the emphasis

was on phase diagrams. The parameters are not as reliable as in most of the other work reported here.

## Th$M$ compounds

Compounds near 50 atomic% appear only in the Co and Ni system, and these are not isomorphous. Crystallographic data for the two follow:

|  | ThCo | ThNi |
|---|---|---|
| $a$ (Å) | 3·74 | 14·51 |
| $b$ (Å) | 10·88 | 4·31 |
| $c$ (Å) | 4·16 | 5·73 |

Extinctions

| | | |
|---|---|---|
| $(hkl)$ | $h+k = 2n+1$ | None |
| $(h0l)$ | $h = 2n+1$, $l = 2n+1$ | None |
| $(hk0)$ | $h+k = 2n+1$ | All, except $h = 4n$ |
| $(0kl)$ | $k = 2n+1$ | $k+l = 2n+1$ |

Space groups

$Cmcm$ or $Cmc$  $\qquad\qquad$ $Pnma$ or $Pn2a$

Cell volumes and approximate composition fix the composition as Th$M$ in each case, with $z = 4$ for ThCo and $z = 8$ for ThNi.

### The structure of ThCo

Neither allowed space group permits an $x$ parameter for fourfold positions, and both intensities and spatial considerations indicate that both Th and Co atoms are in 4($c$) of $Cmcm$:

$$\pm(0, y, \tfrac{1}{4}); \quad \pm(\tfrac{1}{2}, \tfrac{1}{2}+y, \tfrac{1}{4}).$$

The two $y$ parameters were obtained approximately from $P(0, y)$, using $(hk0)$ data. The Fourier synthesis $\varrho(0, y)$ (Fig. 3) was then run, along with the corre-
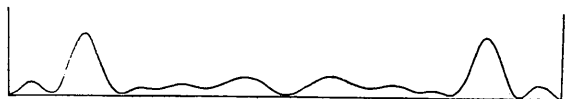


Fig. 3. Section, with $x = 0$, of electron-density projection of ThCo on to (001).

sponding synthetic Fourier, yielding

$$y_{\text{Th}} = 0\cdot136, \quad y_{\text{Co}} = 0\cdot416 .$$

The final parameters led to $R = \Sigma ||F_o| - |F_c|| \div \Sigma |F_o| = 0\cdot14$ for the observed reflections.
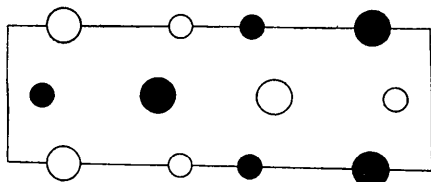


Fig. 4. ThCo atomic positions projected on to (001). Large and small shaded circles: Th and Co atoms with $z = \tfrac{1}{4}$; large and small unshaded circles: Th and Co atoms with $z = \tfrac{3}{4}$.

The structure is illustrated in Fig. 4, and interatomic distances are given in Table 2.

Table 2. *Interatomic distances in* ThCo

| Th | | | Co | | |
|---|---|---|---|---|---|
| | 6 Th | 3·62 Å | | 4 Th | 2·86 Å |
| | 2 Th | 3·74 | | 3 Th | 3·04 |
| | 4 Co | 2·86 | | 2 Co | 2·77 |
| | 3 Co | 3·04 | | | |

### The structure of ThNi

A Patterson projection $P(x, y)$ confirmed the supposition that there were no $y$-parameters, and it can then be shown that all atoms can be placed in set 4($c$) of $Pnma$:

$$\pm(x, \tfrac{1}{4}, z); \quad \pm(\tfrac{1}{2}+x, \tfrac{1}{4}, \tfrac{1}{2}-z) .$$

Approximate parameters from Patterson projections were refined by calculating $\varrho(x, y)$ and $\varrho(y, z)$ at $y = \tfrac{1}{4}$ (Fig. 5), together with corresponding synthetic Fouriers. Final parameters were:
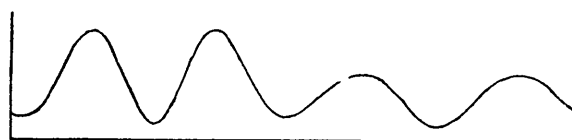
| 4 Th$_1$ | $x_1 = 0\cdot094$ | $z_1 = 0\cdot140$ |
|---|---|---|
| 4 Th$_2$ | $x_2 = 0\cdot344$ | $z_2 = 0\cdot140$ |
| 4 Ni$_3$ | $x_3 = 0\cdot268$ | $z_3 = 0\cdot630$ |
| 4 Ni$_4$ | $x_4 = 0\cdot518$ | $z_4 = 0\cdot870$ , |

for which $R = 0\cdot16$ for the observed reflections.

The structure is illustrated in Fig. 6, and interatomic distances are given in Table 3.
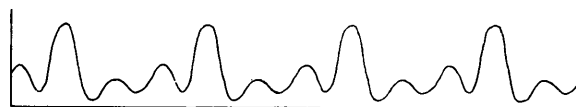


(a)



(b)

Fig. 5. Section, with $y = \tfrac{1}{4}$, of electron-density projection of ThNi (a) on to (001), (b) on to 100.
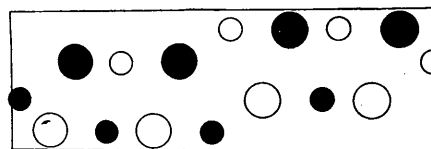


Fig. 6. ThNi atomic positions projected on to (010). Large and small unshaded circles: Th and Ni atoms with $y = \tfrac{1}{4}$; large and small shaded circles: Th and Ni atoms with $y = \tfrac{3}{4}$.

## ThNi$_2$

This phase appears only in the nickel system. It is hexagonal, and isomorphous with the parameterless

#### Table 3. Interatomic distances in ThNi

| | | | | | | |
|---|---|---|---|---|---|---|
| Th$_I$ | 1 Th | 3·54 Å | Ni$_{III}$ | 2 Th | 2·68 Å |
| | 4 Th | 3·70 | | 2 Th | 2·91 |
| | 2 Th | 3·78 | | 1 Th | 3·01 |
| | 2 Th | 3·79 | | 1 Th | 3·11 |
| | 1 Ni | 3·01 | Ni$_{IV}$ | 3 Th | 2·91 |
| | 1 Ni | 3·11 | | 2 Th | 2·98 |
| | 2 Ni | 2·91 | | 1 Th | 3·01 |
| | 2 Ni | 2·98 | | 1 Th | 3·11 |
| Th$_{II}$ | 1 Th | 3·54 | | 2 Ni | 2·69 |
| | 4 Th | 3·70 | | | |
| | 1 Th | 3·79 | | | |
| | 2 Ni | 2·68 | | | |
| | 3 Ni | 2·91 | | | |
| | 1 Ni | 3·01 | | | |
| | 1 Ni | 3·11 | | | |

AlB$_2$ structure. Hence, we list only lattice constants and positions:

$$a = 3·95, \quad c = 3·83 \text{ Å} .$$
1 Th at $(0, 0, 0)$;
2 Ni at $\pm(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$.

Interatomic distances are given in Table 4.

#### Table 4. Interatomic distances in ThNi$_2$

| Th | 12 Ni | 2·99 Å | Ni | 6 Th | 2·99 Å |
|---|---|---|---|---|---|
| | 6 Th | 3·95 | | 3 Ni | 2·29 |
| | 2 Th | 3·83 | | | |

### Compounds of composition near Th$M_3$

The iron and cobalt systems give evidence of compounds somewhere near the composition Th$M_3$, and single crystals of these phases were isolated in both systems from alloys in two-phase regions. Both compounds proved to be hexagonal with Laue symmetry $D_{6h}$, though, in the case of the iron compound, intensity anomalies warrant some caution in concluding that this is the true symmetry. Crystallographic data are:

| | ThFe$_3$ | ThCo$_{2-3}$ |
|---|---|---|
| $a$ (Å) | 5·22 | 5·03 |
| $c$ (Å) | 24·96 | 24·54 |

Extinctions

| | | |
|---|---|---|
| $(HK.0)$ | Except for $H-K=3n$ | Except for $H-K=3n$ |
| $(HH.L)$ | Except for $L=3n$ | When $L=2n+1$ |

In both cases the extinctions suggest that atoms occur in multiples of three. For the iron compound, atomic volumes suggest unit-cell compositions of Th$_6$Fe$_{36}$, Th$_9$Fe$_{27}$ or Th$_{12}$Fe$_{18}$, and only the middle composition seems compatible with the approximately known chemical composition of the phase. The cobalt compound has so much smaller a volume that it appears hard to crowd the same content within the unit cell. We suspect that the composition is really lower in cobalt, but, for reasons outlined below, the composition of the cobalt compound has not been established.

### ThFe$_3$

Because of difficulty in obtaining reliable intensities, no serious attempt was made to determine the structure of ThFe$_3$. However, spatial arguments can be advanced which strongly suggest that the correct space group is $D_{3h}^1$-$C\bar{6}m2$, since in other allowed space groups thorium atoms would necessarily be placed unreasonably close to each other.

### ThCo$_{2-3}$

In obtaining intensity data for this compound it was found that many higher-order reflections were unusually diffuse. On examining these reflections with longer wavelengths it was found that what appeared to be single reflections were now obviously several closely spaced spots. These reflections indicate that the true $c_0$ axis is 8 or 9 times the pseudo axis reported above, i.e. in the neighborhood of 200 Å. This enormous unit cell precluded the possibility of establishing the composition by volume arguments, and discouraged any attempt to obtain further structural information.

### Th$M_5$ compounds

The compounds ThFe$_5$, ThCo$_5$ and ThNi$_5$ were found. All appeared to be isomorphous with the parameterless CaZn$_5$ structure, and this was confirmed by comparing calculated and observed intensities for the nickel compound. The structure has the space group $D_{6h}^1$-$C6/mmm$.

1 Th at $(0, 0, 0)$.
2 $M_1$ at $\pm(\frac{1}{3}, \frac{2}{3}, 0)$.
3 $M_2$ at $(0, \frac{1}{2}, \frac{1}{2})$; $(\frac{1}{2}, 0, \frac{1}{2})$; $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.

Lattice constants for these compounds are:

| | ThFe$_5$ | ThCo$_5$ | ThNi$_5$ |
|---|---|---|---|
| $a_0$ (Å) | 5·13 | 5·01 | 4·97 |
| $c_0$ (Å) | 4·02 | 3·97 | 4·01 |

Interatomic distances are given in Table 5.

#### Table 5. Interatomic distances in Th$M_5$ compounds

| | | ThFe$_5$ | ThCo$_5$ | ThNi$_5$ |
|---|---|---|---|---|
| Th | 6 $M$ | 2·96 Å | 2·89 Å | 2·87 Å |
| | 12 $M$ | 3·27 | 3·21 | 3·20 |
| $M_1$ | 3 Th | 2·96 | 2·89 | 2·87 |
| | 6 $M$ | 2·50 | 2·46 | 2·47 |
| $M_2$ | 4 Th | 3·27 | 3·21 | 3·20 |
| | 4 $M$ | 2·57 | 2·51 | 2·49 |
| | 4 $M$ | 2·50 | 2·46 | 2·47 |

There is some evidence from powder data that the composition of the nickel compound was variable, with a possible range from ThNi$_4$ to ThNi$_5$. This was not examined in detail, however.

## The $Th_2M_{17}$ compounds

In all three systems, compounds occur in the neighborhood of $ThM_{8-9}$, and in all three cases both intensities and positions of lines show that these compounds are very closely related to the $ThM_5$ compounds. Single crystals were obtained of all three, symmetries and space groups were determined, and finally the structures were determined, making use of the known relationships to the $ThM_5$ structure. Because of the large unit cells and large number of reflections involved we have not checked observed and calculated intensities in detail. Since the correspondence with $ThM_5$ compounds was close, the main point is to explain the differences, which the derived structures do.

$Th_2Ni_{17}$ is hexagonal, while $Th_2Fe_{17}$ and $Th_2Co_{17}$ are monoclinic. Since the structure of $Th_2Ni_{17}$ is easier to obtain, and helps somewhat in the discussion of the others, we consider it first.

### $Th_2Ni_{17}$

Powder data indicated a composition near 90 atomic % Ni. Single crystals proved to have a symmetry of $D_{6h}$ with lattice constants

$$a = 8\cdot37, \ c = 8\cdot14 \text{ Å} .$$

The only systematic extinction was $(HH.L)$ for odd $L$, so the allowed space groups are $C6/mmc$, $C6mc$ and $C\bar{6}2c$.

There must be an even number of atoms of each kind per unit cell, and hence either 2, 4 or 6 Th atoms. Atomic and cell volumes then give 40, 34 or 28 for the number of nickel atoms per unit cell, and only the middle composition is close enough to the approximate chemical composition to be acceptable. (Compositions of $Th_4Ni_{32}$ and $Th_4Ni_{36}$ are not strictly excluded by this argument.)

The relation of this unit to that of $ThNi_5$ can be seen by noting that

$$a_{Th_2Ni_{17}} = 8\cdot37 \cong \sqrt{3}\cdot a_{ThNi_5} = 8\cdot60 \text{ Å}$$

and

$$c_{Th_2Ni_{17}} = 8\cdot14 \cong 2c_{ThNi_5} = 8\cdot02 \text{ Å}$$

(see Fig. 7) so that the volume of $Th_2Ni_{17}$ is ∼ six times that of $ThNi_5$, and, without substitution, would contain $Th_6Ni_{30}$. Since the cell contains only 4 Th, and since the atomic volume of Th is ∼ 3 times that for Ni, a substitution of 3 Ni for 1 Th might be expected. However, there is some volume shrinkage on going to $Th_2Ni_{17}$. Spatial arguments then lead to substituting two Ni for one Th, leading to the composition $Th_2Ni_{17}$.

Spatial and symmetry arguments lead to the following structure in $D_{6h}^4-C6/mmc$:

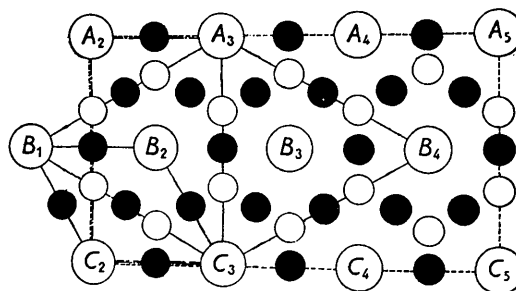2 Th(1) at $\pm(0, 0, \tfrac{1}{4})$;

2 Th(2) at $\pm(\tfrac{1}{3}, \tfrac{2}{3}, \tfrac{3}{4})$;



Fig. 7. Relation of $ThM_5$, $Th_2M_{17}$ and $ThMn_{12}$ structures.

This figure is a projection of the $ThM_5$ structure on to (001), with Th represented by large circles, transition metals by small circles. Solid circles are atoms $\tfrac{1}{2}$ above (or below) the plane of the paper, others are in the plane of the paper. $B_1B_2C_3C_2$ is the unit cell for $ThM_5$.

$A_2A_3C_3C_2$ is the unit cell for the $ThMn_{12}$ structure. It is derived from $ThM_5$ by replacing in alternate layers Th atoms labelled $A$ (and $C$) and Th atoms labelled $B$; each Th is replaced by two Mn atoms with ligand normal to the plane of the figure.

The large hexagonal unit $B_1A_3B_4C_3$ is the unit cell for $Th_2Ni_{17}$. It is formed from $ThNi_5$ by replacing Th atoms $B_2$ in one layer and $B_3$ in the next; each Th atom is replaced by two Ni atoms with ligand normal to the plane of the figure.

The large rectangle $A_2A_5C_5C_2$ is the large monoclinic unit for $Th_2Fe_{17}$ and $Th_2Co_{17}$. It is derived from $ThM_5$ by replacing the Th atoms $B_2$ in the first layer, $B_3$ in the second layer, and $A_3$ in the third layer; each is replaced by two $M$ atoms with their ligand normal to the plane of the figure.

The $TiBe_{12}$ structure (Raeuchle & Rundle, 1952) is also related to these structures but, because of the disorder in $TiBe_{12}$, the exact relationship is not certain.

6 Ni(1) at $(\tfrac{1}{2}, 0, 0)$; $(0, \tfrac{1}{2}, 0)$; $(\tfrac{1}{2}, \tfrac{1}{2}, 0)$; $(\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2})$; $(\tfrac{1}{2}, 0, \tfrac{1}{2})$; $(0, \tfrac{1}{2}, \tfrac{1}{2})$;

12 Ni(2) at $\pm(x, 0, \tfrac{1}{4})$; $\pm(0, x, \tfrac{1}{4})$; $\pm(x, x, \tfrac{1}{4})$; $\pm(\bar{x}, 0, \tfrac{1}{4})$; $\pm(0, \bar{x}, \tfrac{1}{4})$; $\pm(\bar{x}, \bar{x}, \tfrac{1}{4})$, with $x_2 = \tfrac{1}{3}$;

12 Ni(3) at $\pm(x, 2x, 0)$; $\pm(\bar{x}, x, 0)$; $\pm(2x, x, 0)$; $\pm(x, 2x, \tfrac{1}{2})$; $\pm(\bar{x}, x, \tfrac{1}{2})$; $\pm(x, 2x, \tfrac{1}{2})$, with $x_3 = \tfrac{1}{6}$;

4 Ni(4) at $\pm(\tfrac{1}{3}, \tfrac{2}{3}, z)$; $\pm(\tfrac{1}{3}, 2, \tfrac{1}{2}-z)$, with $z_4 = 0\cdot11$.

The Ni(4) positions replace 2 Th atoms, and $z_4$ was chosen to give satisfactory interatomic distances. No serious attempt was made to get this parameter from intensities because of the low scattering power of the few nickel atoms involved. Other nickel parameters are ideal ones derived from the relation between $ThNi_5$ and $Th_2Ni_{17}$, and distortion may alter them somewhat.

### $Th_2Fe_{17}$ and $Th_2Co_{17}$

Powder diagrams reveal phases in the Fe and Co systems at about 90 atomic % transition metal. Single crystals of these phases proved to be monoclinic with lattice constants:

| | $Th_2Fe_{17}$ | $Th_2Co_{17}$ |
|---|---|---|
| $a$ (Å) | 9·68 | 9·62 |
| $b$ (Å) | 8·56 | 8·46 |
| $c$ (Å) | 6·46 | 6·32 |
| $\beta$ | 99° 20′ | 99° 06′ |

The only extinction was $(hkl)$ with $(h+k)$ odd. Possible space groups are $C2/m$, $Cm$ and $C2$.

Atomic and unit-cell volumes, together with the rough chemical composition, lead to the conclusion that there are 4 Th per unit cell and 34–36 $M$ atoms. The final composition was chosen when the similarity to $ThM_5$ compounds was recognized. Substituting 2 Fe or 2 Co for 1 Th in the $ThM_5$ structure, in the manner outlined below, gives the monoclinic structure, and it was decided that 2 $M$ atoms replace 1 Th atom by analogy with $Th_2Ni_{17}$ (above) and $ThMn_{12}$ (see below).

A Patterson projection, $P(x, z)$ was prepared (Fig. 8), and from this it was concluded that the thorium positions were $(0, 0, 0)$, $(\frac{1}{2}, \frac{1}{2}, 0)\pm(x, 0, z)$, with $x=\frac{1}{6}$, $z = \frac{1}{3}$, and the suggested arrangement of $M$ atoms resembled the $ThM_5$ structure.

The relation to the $ThM_5$ structure is made more obvious by choosing a larger monoclinic cell, which for $Th_2Fe_{17}$ is (Fig. 7),
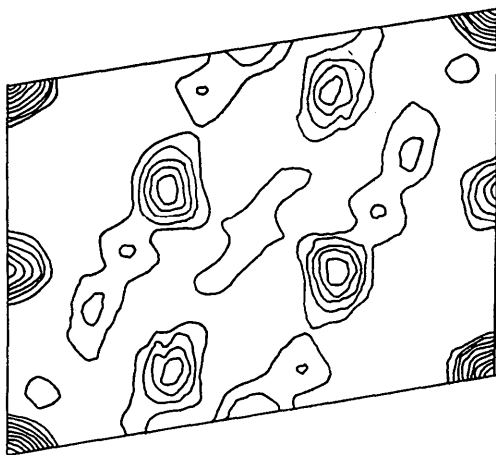


Fig. 8. Patterson projection of $Th_2Fe_{17}$ on to (010).

$$a' = 14\cdot86, \quad b' = 8\cdot56, \quad c' = 12\cdot47 \text{ Å}, \quad \beta = 90°,$$

where

$$a' \cong 3a_{ThFe_5}, \quad b' \cong \sqrt{3}.a_{ThFe_5} \quad \text{and} \quad c' \cong 3c_{ThFe_5}.$$

The type of substitution in the larger unit cell, consistent with the thorium positions of the smaller unit, is described under Fig. 7, and is best seen there. The atomic positions in the smaller unit are based on $C2/m$:

$(0, 0, 0)$; $(\frac{1}{2}, \frac{1}{2}, 0)+$

4 Th at $4(i)$: $(x, 0, z)$; $(\bar{x}, 0, \bar{z})$, with $x=\frac{1}{6}$, $z=\frac{1}{3}$;

8 $Fe_1$ at $8(j)$: $(x, y, z)$; $(x, \bar{y}, z)$; $(\bar{x}, y, \bar{z})$; $(\bar{x}, \bar{y}, \bar{z})$, with $x_1=\frac{1}{6}$, $y_1=0\cdot360$, $z_1=\frac{1}{3}$;

8 $Fe_2$ at $8(j)$, with $x_2=0\cdot417$, $y_2=\frac{1}{4}$, $z_2=\frac{1}{3}$;

4 $Fe_3$ at $4(g)$: $(0, y, 0)$; $(0, \bar{y}, 0)$, with $y_3=0\cdot140$;

4 $Fe_4$ at $4(e)$: $(\frac{1}{4}, \frac{1}{4}, 0)$; $(\frac{1}{4}, \frac{3}{4}, 0)$;

4 $Fe_5$ at $4(i)$, with $x_5=\frac{1}{6}$, $z_5=\frac{2}{3}$;

4 $Fe_6$ at $4(i)$, with $x_6=0\cdot416$, $z_6=0\cdot147$;

2 $Fe_7$ at $2(d)$: $(0, \frac{1}{2}, \frac{1}{2})$.

### Relation to $ThMn_{12}$

The hexagonal and monoclinic $Th_2M_{17}$ compounds are related to the $ThM_5$ ($CaZn_5$-type) structure, as shown in Fig. 7, by substituting in an orderly way 2 $M$ atoms for 1 Th atom, and in every case the 2 $M$ atoms substituted for Th have their axis along $c_0$ of the original hexagonal cell. The tetragonal $ThMn_{12}$ structure is related to the $ThM_5$ structure in a similar way, but by different ordering of the substitution into a hypothetical $ThMn_5$ structure. The compound $ThMn_5$ is unknown. The relation among these compounds is shown in Fig. 7.

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