trichloride, and subsequent hydrolysis at room temperature. This sample was labelled form I.

By slow evaporation at room temperature of a solution of form I in an ethanol–water mixture, different crystals were obtained; these were labelled form II.

Rotation, Weissenberg and precession photographs were obtained with Ni-filtered Cu *K* radiation.

The crystal data are as follows:

Form I:
System monoclinic
Space group either *Cc* or *C*2/*c* from the following systematic absences:

hkl for $h+k=2n+1$
$h0l$ for $l=2n+1$.
$a=49{\cdot}6\pm0{\cdot}1$ Å
$b=\ 5{\cdot}5\pm0{\cdot}1$
$c=13{\cdot}2\pm0{\cdot}1$
$\beta=93°$
$Z=16$
$D_x=1{\cdot}44$ g.cm^{-3}
D_m (pycnometer) $=1{\cdot}43\pm0{\cdot}01$ g.cm^{-3} .

The crystals grew in the form of very small needles.

Form II
System: monoclinic
Space group $P2_1/a$ from the following systematic absences:

$h0l$ for $h=2n+1$
$0k0$ for $k=2n+1$
$a=28{\cdot}4\pm0{\cdot}1$ Å
$b=\ 5{\cdot}2\pm0{\cdot}1$
$c=12{\cdot}7\pm0{\cdot}1$
$\beta=92°30'$
$Z=8$
$D_x=1{\cdot}38$ g.cm^{-3}
D_m (flotation) $=1{\cdot}35\pm0{\cdot}01$ g.cm^{-3} .

The crystals grew in the form of needles.

The powder data for both forms are being submitted for inclusion in the ASTM X-ray Powder Data File.

Micro-melting points were determined on a Kofler hot stage to characterize both kind of crystals. Two different behaviours were observed: crystals of form I melt without decomposition at 168 °C; some sublimation is observed. On the other hand when crystals of form II are gradually heated a strong sublimation is observed and, at about 80 °C, the crystals alter, cracking and becoming opaque; the altered crystals melt at 168 °C.

If crystals of form II are placed on a hot stage preheated to about 100 °C, their melting at 125 °C can be observed; on continued heating, small crystals appear in the molten mass which grow slowly and melt at 168 °C.

Through the introduction of a solution phase it was possible to observe the passage of form I to form II and *vice versa*. When a saturated solution of the substance in nitrobenzene kept at 65 °C was seeded with one crystal of each form, the crystals of form I grew while the crystals of form II dissolved. When the test was repeated at 32 °C the process was reversed, the form II crystals growing, while the form I crystals disappeared.

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Note on the structures of $TbFe_2$ and $TbFe_3$.

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By means of single-crystal X-ray diffraction methods the existence of $TbFe_3$ ($R\bar{3}m$, $PuNi_3$-type) $a=8{\cdot}48$ Å, $\alpha=34°20'$ has been established and that of the previously reported $TbFe_2$ ($Fd3m$, $MgCu_2$-type) $a=7{\cdot}40$ Å has been confirmed. Similar investigation of alloys of composition intermediate between the two compounds shows $TbFe_3$ to exist over a range of composition.

Recently Smith & Hansen (1965), by single-crystal techniques, found that the crystal structures of YNi_3, YCo_3, $ThFe_3$ and $GdFe_3$ are all isotypic with $PuNi_3$ ($R\bar{3}m$) (Cromer & Olsen, 1959). Furthermore, these authors were able to show that the erroneous interpretation of the structures by the previous investigators (Florio, Baenziger & Rundle, 1956) was due to the fault-stacking and twinning inherent to these compounds. Concurrently, based on powder pattern methods, GdX_3 and YX_3 (X = Fe, Co, Ni) (Van Vucht, 1965) and RCo_3 (R = Y, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er and Tm) (Bertaut, Lemaire & Schweizer, 1965) have all been identified as isotypic with $PuNi_3$ ($R\bar{3}m$). Also, it has been shown by means of powder pattern methods (Dwight, 1961; Novy, Vickery & Kleber, 1961; Kripyakevich, Teslyuk & Frankevich, 1965) that all the AB_2 compounds found in the R–X (R = rare earth, X = Fe, Co and Ni) systems are of the *C*15 ($MgCu_2$) type. These facts suggest that RX_2 ($Fd3m$) and RX_3 ($R\bar{3}m$) compounds coexist in the R–X systems.

A close comparison of the crystal structures of RX_2 and RX_3 compounds shows (1) the tetrahedral clustering of the X atoms as well as the stacking of these tetrahedral units in the two structures are closely related (Fig. 1) and (2) the hexagonal arrangements of the R atoms in the two structures have a common stacking sequence, *ABCABC*; the only difference is that the hexagonal array of R atoms is double layered in RX_2 and triple layered in RX_3. Inasmuch as the c/a (hexagonal representation) ratio of RX_3 compounds (4·84) is about twice that of RX_2 coumponds (2·45) and the atomic arrangements are closely related, the powder patterns of the two types of compounds are necessarily similar. This implies that it is possible to misidentify RX_3 as RX_2 based on powder pattern methods. Parallel to these

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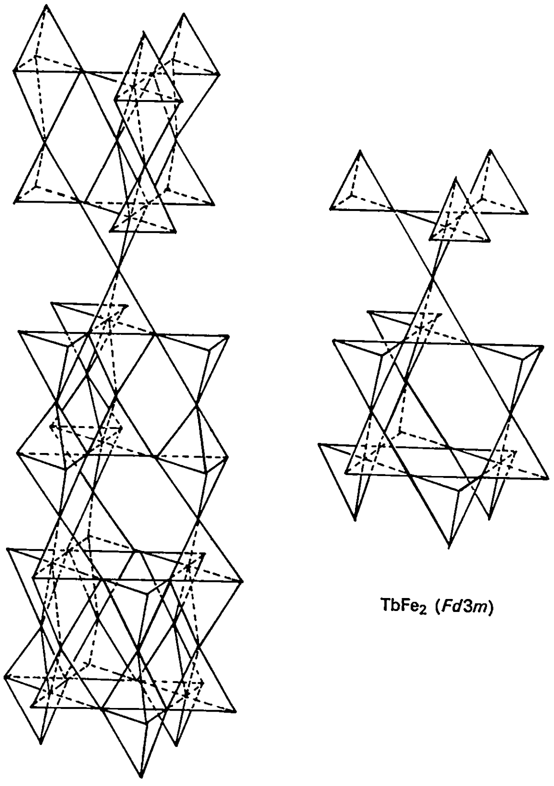
observations is the fact that Florio *et al.* (1956) did not find '$ThFe_2$' or '$ThCo_2$' in their single-crystal work on the Th–X systems in which $ThFe_3$ and $ThCo_3$ were identified and later characterized by Smith & Hansen (1965).

For these reasons, it is desirable to establish the existence of the RX_2 ($MgCu_2$-type) compounds by single-crystal methods and to investigate alloys in the composition range between RX_2 and RX_3 for a possible faulted composite structure. Because the existence of $GdFe_3$ has been confirmed and Tb is next to Gd in atomic number, the present investigation covers the Tb–Fe system in the composition range Fe/Tb = 1·5 through 3·0.

The elements were alloyed together in a zirconia (ZrO_2) bomb which in turn was placed inside a 15-mm wall thickness graphite crucible equipped with a lid. The whole assembly was heated in a high-frequency induction heating unit under an argon atmosphere. Although the Tb–Fe phase diagram has not been investigated, the Gd–Fe phase diagram is known (Copeland, Krug, Armantrout & Kato, 1962) and both $GdFe_3$ and $GdFe_2$ are peritectic compounds. Assuming the Tb–Fe phase diagram to be essentially the same as that of the Gd–Fe system, it is obvious that annealing is required in forming these alloys. However, the narrow temperature range (70°C) between the peritectic temperatures of $GdFe_3$ (1150°C) and of $GdFe_2$ (1080°C) and a lack of knowledge of the precise temperature inside the zirconia bomb in the present set up prevented us from carrying out reliable annealing. However, this deficiency was offset by the fact that all the X-ray investigations were performed on single crystals.


$TbFe_3$ ($R\bar{3}m$)

$TbFe_2$ ($Fd3m$)

Fig. 1. Atomic arrangement of Fe in $TbFe_3$ and $TbFe_2$; Fe atoms are located at the nodes.

Four alloys were prepared with the atomic ratios Fe/Tb = 1·5, 2·0, 2·5 and 3·0 (hereafter referred to as alloys 1, 2, 3 and 4), with 5 g of Tb metal in each charge. These alloys are fairly brittle and slowly decompose in open air. Morphologically, alloys 3 and 4 are in platelet form whereas 1 and 2 are irregular in shape.

Single crystals of approximately spherical shape (approximate diameter 0·03 mm), obtained from alloy 4 showed Laue symmetry $\bar{3}m$. Zr-filtered Mo radiation and a Buerger precession camera were used to collect intensity data. With b^* (reciprocal axis in hexagonal representation) aligned along the X-ray beam, six layers ($0 \leq k \leq 5$) of precession photographs were obtained which yielded a total of 183 symmetry independent reflections. The systematic extinctions in these data gave the probable hexagonal space groups $R32$, $R3m$ and $R\bar{3}m$ and the cell parameters:

rhombohedral $a = 8{\cdot}48 \pm 0{\cdot}03$ Å, $\alpha = 34°20' \pm 11'$
hexagonal $a = 5{\cdot}11 \pm 0{\cdot}02$ Å, $c = 24{\cdot}42 \pm 0{\cdot}08$ Å .

Although these preliminary crystallographic data strongly suggest that this compound is isostructural with other RX_3 compounds (Smith & Hansen, 1965), in view of the purpose described for this investigation the structure determination was carried out without any prior assumption.

The conversion of the intensity data to $k|F_o|^2$ was carried out in the same manner as described in the identification of Gd_6Mn_{23} (Wang, Gilfrich, Ernst & Hubbard, 1964). The atomic scattering factors given by Thomas & Umeda (1957) were used and no dispersion corrections were applied. A complete analysis of the peak positions and peak heights observed in a three-dimensional Patterson synthesis calculated using the X-ray 63 System (University of Maryland Computer Science Center, 1964) yielded 9 Tb and 24 Fe atoms. The atomic arrangement showed the crystal structure to be centrosymmetric and consequently the space group to be $R\bar{3}m$. The ensuing Fourier synthesis, based on the observed absolute structure factors and the calculated phases, indicated positions for three additional Fe atoms. This is a total of 9 Tb and 27 Fe atoms or nine $TbFe_3$ formula weights per unit cell (hexagonal) in complete agreement with the results of Smith & Hansen (1965) on other RX_3 compounds. After three cycles of full-matrix isotropic least-squares refinement including the 65 unobserved reflections, an agreement factor $R(F) = \Sigma\, ||F_o| - |F_c|| / \Sigma\, |F_o|$ of

Table 1. *Atomic positional parameters of* $TbFe_3$

Atom	x	y	z	B^* (isotropic)
3 Tb(a)	0	0	0	1·1
6 Tb(c)	0	0	0·1414 (±0·0002)	1·2
3 Fe(b)	0	0	0·5	1·7
6 Fe(c)	0	0	0·6659 (±0·0003)	2·1
18 Fe(h)	0·5023 (±0·0014)	$-x$	0·0814 (±0·0002)	1·9

* Average standard deviation = ±0·3.

Table 2. *Interatomic distances in* TbFe$_3$

Average standard deviations: Tb–Tb ±0·03 Å
Tb–Fe ±0·03
Fe–Fe ±0·04

Tb(*a*)—2 Tb(*c*)	3·45 Å	Fe(*c*)–3 Tb(*a*)	—
—6 Fe(*c*)	2·95	–3 Fe(*c*)	2·95
–12 Fe(*h*)	3·28	–3 Fe(*h*)	2·53
		–3 Fe(*h*)	2·54
Tb(*c*)—1 Tb(*a*)	—		
—3 Tb(*c*)	3·21	Fe(*h*)–2 Tb(*a*)	—
—3 Fe(*b*)	3·01	–2 Tb(*c*)	—
—3 Fe(*h*)	3·08	–1 Fe(*b*)	—
—6 Fe(*h*)	2·91	–2 Fe(*c*)	—
		–4 Fe(*h*)	2·56
Fe(*b*)—3 Tb(*c*)	—		
—6 Fe(*h*)	2·54		

0·13 was obtained. The final atomic coordinates and interatomic distances are given in Tables 1 and 2 respectively.*

Several crystals were obtained from both the top and bottom portions of alloys 2 and 3. These crystals all showed diffraction symmetry, $\bar{3}m$ rhombohedral. This indicates that the alloys in this composition range were predominantly TbFe$_3$, probably owing to improper annealing. Precession photographs of these single crystals show lattice constants of the same order of magnitude as those found for TbFe$_3$, but expanding noticeably as the alloy composition becomes richer in Tb [$a=5{\cdot}12$, $c=24{\cdot}64$ Å for alloy 3 and $a=5{\cdot}14$, $c=24{\cdot}94$ Å for alloy 2 compared with $a=5{\cdot}11$, $c=24{\cdot}42$ Å for TbFe$_3$ (alloy 4)]. Further, side by side comparison of these photographs with those of TbFe$_3$ revealed a considerable change in the relative intensities of certain reflections. These facts imply that certain Fe atoms in TbFe$_3$ are replaced in either an orderly or a disorderly manner with Tb atoms as the alloy composition becomes richer in Tb. Complete intensity data from these crystals are being collected and the manner in which Fe atoms are replaced by Tb atoms is under investigation.

The crystals obtained from alloy 1 are cubic with diffraction symmetry $m3m$. Four levels ($0 \le l \le 3$) of precession photographs gave a f.c.c. extinction pattern and a lattice constant, $a=7{\cdot}40$ Å. The intensities of the 22 symmetry independent reflections agreed ($R(F)=0{\cdot}08$) with those calculated from the atomic positional parameters and the space group $Fd3m$ given for MgCu$_2$. This, therefore, substantiated the existence of TbFe$_2$ (MgCu$_2$ type) (Kripyakevich *et al.*, 1965) and other RX$_2$ compounds (Novy *et al.*, 1961) reported previously based on powder pattern methods. This implies that the MgCu$_2$ type Laves phase indeed exists in all the R–X systems (the Pm–X and Eu–X are the only systems yet to be investigated). However, this fact is at odds with the postulate (Laves & Witte, 1936; Witte, 1952; Dwight, 1961; Elliott, 1964) that a Laves phase is sensitive to the valence electron concentration which effectively controls the stability of the given Laves phase: *C*14 (MgZn$_2$), *C*15 (MgCu$_2$) and *C*36 (MgNi$_2$) type.

The experiments show that TbFe$_3$ is not a single composition compound but has a certain solubility range. Since replacing a set of 3 Fe atoms in TbFe$_3$ ($R\bar{3}m$) with Tb atoms is essentially equivalent to altering the Fe/Tb atomic ratio from 3 to 2 (9TbFe$_3$→12TbFe$_2$) while retaining the crystal symmetry, the solubility range of TbFe$_3$ is not unreasonable. Logically, such replacements should make the atomic arrangement in '12TbFe$_2$ ($R\bar{3}m$)' become more similar to that in TbFe$_2$ ($Fd3m$). This is currently under investigation.

The relative stability of AB$_3$ (PuNi$_3$-type) compounds as compared with AB$_2$ (MgCu$_2$-type) compounds is far from clear. In the Pu–Fe system, PuFe$_2$ is present but 'PuFe$_3$' is absent (Elliott, 1965) despite the fact that both types of compound are found to exist in the Pu–Co and Pu–Ni systems. In sharp contrast to this are the Th–X systems (X = Fe and Co) in which the ThX$_3$ (PuNi$_3$ type) is present but 'ThX$_2$' (MgCu$_2$ type) is absent (Florio *et al.*, 1956; Smith & Hansen, 1965). Nonetheless, it should be noted that in the systems in which the AB$_3$ phase (PuNi$_3$ type) is accompanied by an AB$_2$ phase (*e.g.*, Pu–Ni and the confirmed R–X systems), the AB$_2$ phase is invariably a Laves phase of the *C*15 (MgCu$_2$ type) and not of the *C*14 or *C*36-type. In view of these facts, while it is reasonable to assume that PuNi$_3$-type compounds exist in all R–X systems, the final confirmation must await further experimental results.

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* Inasmuch as neither the crystal structure of TbFe$_3$ nor TbFe$_2$ reported here is the first of its kind, observed and calculated structure factors are not included in this communication.