Acta Cryst. (1965). **19**, 1019

The Structures of YNi_3, YCo_3, $ThFe_3$ and $GdFe_3$*

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(*Received* 8 *April* 1965)

The crystal structures of YNi_3, YCo_3, $ThFe_3$, and $GdFe_3$ have been found to be isostructural with $PuNi_3$ in space group $R\bar{3}m$. The determinations for the first three of these phases were based on single-crystal data while the determination of the $GdFe_3$ structure was based on previously published intensity data taken from a polycrystalline specimen. There is evidence that these rhombohedral structures are susceptible to faulting with the stacking faults occurring normal to the c axis. Lattice parameters in the hexagonal representation were determined to be: $a_0 = 4{\cdot}9779 \pm 0{\cdot}0004$, $c_0 = 24{\cdot}449 \pm 0{\cdot}003$ Å for YNi_3; $a_0 = 5{\cdot}020 \pm 0{\cdot}005$, $c_0 = 24{\cdot}40 \pm 0{\cdot}03$ Å for YCo_3; and $a = 5{\cdot}18 \pm 0{\cdot}03$, $c = 25{\cdot}2 \pm 0{\cdot}3$ Å for $ThFe_3$.

Introduction

In an investigation of the yttrium–nickel system, Beaudry & Daane (1960) noted the existence of nine intermetallic compounds. Their work indicates that YNi_2 crystallizes in the $C15$ ($MgCu_2$) structure, YNi_5 crystallizes in the D_{2d} ($CaZn_5$) structure, and Y_2Ni_{17} crystallizes with the Th_2Ni_{17} structure (Florio, Baenziger & Rundle, 1956). Walline & Wallace (1964) report that YNi crystallizes in the $B27$ (FeB) structure though a determination (Smith & Hansen, 1965) of the atomic coordinates shows that the positional parameters require monoclinic symmetry rather than orthorhombic symmetry and thus the structure represents a minor distortion of the prototype (FeB) structure. Beaudry & Daane (1960) also reported the diffraction symmetry and lattice parameters of a single crystal of YNi_3. No additional crystallographic information is available for the yttrium–nickel compounds, and it was on this basis that the present investigation of the structure of YNi_3 was undertaken. The results from YNi_3 prompted investigation of the YCo_3 and $ThFe_3$ structures, and data recorded by Copeland, Krug, Armantrout & Kato (1962) were sufficiently complete to allow extension of the investigation to $GdFe_3$.

YNi_3

A single crystal was selected from an yttrium–nickel alloy containing 31 at.% yttrium; this alloy had been prepared by arc melting and had been subsequently fragmented by a single blow in a diamond mortar. The crystal was in the form of a platelet with hexagonal cross-section. Because of the initial large size, the crystal dimensions were reduced by grinding in a sphere grinder of the type described by Whitmore (1954); the final shape was not spherical but was a disc with rounded edges. The disc was ~1 mm in diameter by ~0·5 mm thick. Transmission Laue patterns showed a threefold axis normal to the disc face. Cubic symmetry was precluded by the absence of additional threefold axes at the symmetry-related angular coordinates, and the reflections were then indexed on the basis of a hexagonal unit cell. The symmetry and characteristic extinctions which were observed in Weissenberg patterns of the levels $kh0$ through $hk6$ and in precession patterns of the levels $0kl$, $1kl$, $2kl$, and hkl combine to indicate the probable space group to be $R\bar{3}m$, $R32$ or $R3m$. The Weissenberg data were taken with Cu $K\alpha$ radiation and the precession data with Ag $K\alpha$ radiation. It should be noted, because of later relevance to the interpretation of the $ThFe_3$ structure, that the $hk6$ layer exhibited $6m$ symmetry and also that the intensities of the $hk3$ reflections were extremely weak, only two or three reflections being discernible after a forty-eight hour exposure.

Precision lattice parameters for the hexagonal unit cell were determined with a General Electric Single Crystal Orienter and Cu $K\alpha$ radiation. The wave length of Cu $K\alpha_1$ was taken to be 1·5405 Å. Values from four $hk0$ reflections in the range $32° < \theta < 68°$ were extrapolated against the Nelson–Riley (1945) function to obtain $a_0 = 4{\cdot}9779 \pm 0{\cdot}0004$ Å and a similar extrapolation based on eleven $00l$ reflections in the range $16° < \theta < 71°$ yielded a value of $c_0 = 24{\cdot}449 \pm 0{\cdot}003$ Å. The corresponding rhombohedral parameters are $a_0 = 8{\cdot}6416 \pm 0{\cdot}0009$ Å and $\alpha_0 = 33{\cdot}48 \pm 0{\cdot}01°$. The agreement in symmetry and lattice parameters with those reported by Beaudry & Daane (1960) confirm that the crystal under investigation was indeed the phase which they identified as YNi_3.

Intensity data for ninety-six independent reflections of the types hkl and $h0l$ were accumulated by visual comparison of timed exposures (Buerger, 1960) taken with a precession camera and Ag $K\alpha$ radiation. An additional fifty-two reflections in the measurable region were unobserved. Standard corrections were made for Lorentz and polarization effects. Since the orientation of the crystal was such that the integrated path lengths for hhl and $h0l$ reflections did not vary greatly in precession data and since the mass absorption coefficient

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* Contribution No. 1694. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

Table 1. *Comparison of observed and calculated structure factors for* YNi$_3$, YCo$_3$ *and* ThFe$_3$

hkℓ	$\lvert F_o \rvert$	F_c	hkℓ	$\lvert F_o \rvert$	F_c	hkℓ	$\lvert F_o \rvert$	F_c	hkℓ	$\lvert F_o \rvert$	F_c
YNi$_3$											
0,0,15	23.9	23.6	3,3,18	<1.6	6.0	3,0,24	<1.5	2.2	1,0,$\overline{17}$	2.5	-3.6
0,0,18	14.2	-15.4	3,3,21	8.7	10.5	3,0,27	4.4	3.6	1,0,$\overline{20}$	11.4	10.6
0,0,21	12.3	11.1	3,3,24	<1.5	1.7	3,0,30	16.7	15.6	1,0,$\overline{23}$	<1.4	-2.0
0,0,24	24.1	21.6	3,3,27	<1.4	2.1	3,0,33	<1.2	-1.2	1,0,$\overline{26}$	7.3	-6.2
0,0,27	10.5	9.2	3,3,30	13.7	12.2	4,0,1	20.6	21.1	1,0,$\overline{29}$	9.6	8.6
0,0,30	<1.5	1.7	4,4,3	<1.5	-1.4	4,0,4	12.8	-13.4	1,0,$\overline{32}$	<1.5	0.0
0,0,36	28.4	22.6	4,4,6	<1.5	0.9	4,0,7	8.7	-9.0	1,0,$\overline{35}$	<1.5	0.5
1,1,3	<0.9	-0.8	4,4,9	<1.4	2.7	4,0,10	2.8	4.2	2,0,$\overline{4}$	18.5	-19.1
1,1,6	34.9	37.1	1,0,10	7.8	-7.7	4,0,13	17.1	16.1	2,0,$\overline{10}$	8.8	6.4
1,1,9	11.1	11.5	1,0,13	7.1	-6.1	4,0,16	<1.8	0.3	2,0,$\overline{13}$	21.9	21.7
1,1,12	<1.2	3.7	1,0,16	10.4	10.2	4,0,19	18.0	-20.4	2,0,$\overline{16}$	<1.3	0.1
1,1,15	15.0	16.9	1,0,19	<1.3	-3.0	4,0,22	12.0	13.8	2,0,$\overline{19}$	24.6	-25.5
1,1,18	10.4	10.5	1,0,22	12.6	11.1	4,0,25	2.2	2.8	2,0,$\overline{22}$	15.8	16.6
1,1,21	15.5	15.7	1,0,25	17.4	-15.0	4,0,28	3.7	5.1	2,0,$\overline{25}$	3.7	4.1
1,1,24	<1.5	2.8	1,0,28	13.5	10.0	4,0,31	13.0	-12.5	2,0,$\overline{28}$	5.3	5.8
1,1,27	<1.5	3.4	1,0,31	<1.5	0.1	4,0,34	<1.0	2.1	2,0,$\overline{31}$	15.3	-14.7
1,1,30	18.3	16.7	1,0,34	<1.5	0.5	5,0,2	<1.5	0.9	2,0,$\overline{34}$	<1.5	2.5
1,1,33	<1.5	-0.7	1,0,37	<1.4	-0.6	5,0,5	<1.5	0.3	4,0,$\overline{2}$	14.7	13.0
1,1,36	12.3	10.3	2,0,2	20.5	19.4	5,0,8	11.7	12.2	4,0,$\overline{5}$	20.0	-21.1
2,2,0	51.0	48.5	2,0,5	37.0	-30.4	5,0,11	12.8	-14.1	4,0,$\overline{8}$	<1.4	1.7
2,2,3	<1.2	-0.3	2,0,8	<0.9	1.5	5,0,14	8.2	8.7	4,0,$\overline{11}$	<1.4	2.7
2,2,6	<1.3	0.1	2,0,11	6.1	4.8	5,0,17	<1.6	-2.2	4,0,$\overline{14}$	22.6	22.3
2,2,9	5.3	6.0	2,0,14	29.4	29.1	5,0,20	5.4	6.1	4,0,$\overline{17}$	17.1	-17.9
2,2,12	27.2	26.9	2,0,17	22.2	-22.7	5,0,23	<1.5	-2.1	4,0,$\overline{20}$	<1.5	-4.5
2,2,15	15.5	17.5	2,0,20	5.6	-5.8	5,0,26	<1.5	-3.9	4,0,$\overline{23}$	12.0	10.1
2,2,18	11.4	-12.0	2,0,23	12.2	12.6	5,0,29	6.6	6.9	4,0,$\overline{26}$	5.4	5.9
2,2,21	9.5	8.9	2,0,26	8.2	7.5	6,0,0	25.4	29.9	4,0,$\overline{29}$	<1.5	1.8
2,2,24	18.1	18.7	2,0,29	<1.5	-2.4	6,0,3	<1.6	-1.1	5,0,$\overline{1}$	<1.5	-1.5
2,2,27	8.2	7.3	2,0,32	12.8	-11.3	6,0,6	<1.6	0.7	5,0,$\overline{4}$	<1.5	-2.8
2,2,30	<1.5	1.7	3,0,0	22.4	21.6	6,0,9	<1.6	3.4	5,0,$\overline{7}$	11.7	11.5
2,2,33	<1.5	-5.3	3,0,3	<1.2	0.0	6,0,12	15.7	16.8	5,0,$\overline{10}$	<1.5	3.3
3,3,0	13.6	14.9	3,0,6	30.2	30.0	6,0,15	10.9	11.7	5,0,$\overline{13}$	<1.5	-4.0
3,3,3	<1.5	-1.6	3,0,9	9.6	8.3	6,0,18	8.2	-8.4	5,0,$\overline{16}$	4.4	5.2
3,3,6	19.3	20.0	3,0,12	<1.3	2.8	6,0,21	5.7	6.4	5,0,$\overline{19}$	<1.6	-2.3
3,3,9	4.4	6.0	3,0,15	14.9	15.5	6,0,24	13.0	12.9	5,0,$\overline{22}$	8.2	9.0
3,3,12	<1.5	1.9	3,0,18	9.0	9.2	1,0,$\overline{11}$	21.4	-22.1	5,0,$\overline{25}$	9.5	-11.2
3,3,15	8.9	10.6	3,0,21	13.3	13.3	1,0,$\overline{14}$	10.6	11.7	5,0,$\overline{28}$	6.2	6.6
YCo$_3$											
0,0,15	11.7	9.9	1,1,12	2.3	1.9	2,2,9	<1.3	1.9	3,3,9	2.2	2.7
0,0,18	6.3	-5.6	1,1,15	6.6	6.1	2,2,12	10.5	10.4	3,3,12	<1.5	1.5
0,0,21	4.4	3.7	1,1,18	4.6	3.9	2,2,15	6.9	7.6	3,3,15	3.8	4.3
0,0,24	7.6	8.3	1,1,21	7.8	7.0	2,2,18	4.1	-4.3	3,3,18	<1.5	2.2
0,0,27	6.0	5.9	1,1,24	<1.5	0.7	2,2,21	3.0	3.2	3,3,21	4.7	5.0
0,0,30	<1.5	0.3	1,1,27	2.1	2.1	2,2,24	7.2	6.6	3,3,24	<1.5	0.7
0,0,33	2.7	-2.5	1,1,30	6.5	5.8	2,2,27	4.7	5.0	3,3,27	<1.4	1.9
0,0,36	9.5	8.5	1,1,33	<1.5	1.2	2,2,30	<1.5	0.4	3,3,30	3.8	4.1
1,1,0	10.2	10.5	1,1,36	4.5	4.0	2,2,33	<1.5	-2.1	4,4,0	8.5	9.6
1,1,3	<0.9	-0.4	2,2,0	17.0	18.3	2,2,36	7.7	7.4	4,4,3	<1.5	0.2
1,1,6	14.4	14.1	2,2,3	<1.2	0.3	3,3,0	5.4	6.2	4,4,6	<1.5	0.8
1,1,9	4.7	4.4	2,2,6	<1.3	0.5	3,3,3	<1.5	-0.2	4,4,9	<1.4	1.4
						3,3,6	7.5	7.4	4,4,12	5.1	5.6
ThFe$_3$											
0,0,9	3.4	2.4	3,0,3	<1.1	1.2	5,0,2	<1.5	3.3	2,0,$\overline{10}$	<1.1	-1.2
0,0,12	10.7	9.7	3,0,6	12.7	12.5	5,0,5	<1.5	3.5	2,0,$\overline{13}$	9.3	10.1
0,0,15	13.0	11.7	3,0,9	<1.2	0.9	5,0,8	5.1	5.3	4,0,$\overline{2}$	<1.4	3.7
1,0,7	13.4	12.2	3,0,12	<1.3	0.7	6,0,0	9.9	9.5	4,0,$\overline{5}$	<1.4	-1.6
2,0,2	4.5	5.4	3,0,15	7.2	9.8	1,0,$\overline{8}$	13.2	12.0	4,0,$\overline{8}$	<1.4	5.0
2,0,5	4.3	-4.5	4,0,1	7.4	8.0	1,0,$\overline{11}$	6.7	-5.8	4,0,$\overline{11}$	<1.4	-2.4
2,0,8	4.2	5.3	4,0,4	<1.4	-3.8	1,0,$\overline{14}$	9.1	8.2	4,0,$\overline{14}$	9.7	10.2
2,0,11	<1.1	-1.7	4,0,7	<1.4	5.7	2,0,$\overline{1}$	12.9	12.1	5,0,$\overline{1}$	<1.5	2.2
2,0,14	11.0	13.2	4,0,10	<1.4	-0.9	2,0,$\overline{4}$	6.0	-5.3	5,0,$\overline{4}$	<1.5	-4.2
3,0,0	10.0	11.2	4,0,13	6.3	7.2	2,0,$\overline{7}$	3.5	4.8	5,0,$\overline{7}$	9.9	9.8

of 34·6 $cm^2.g^{-1}$ for Ag $K\alpha$ radiation is not large, no absorption corrections were applied. The $PuNi_3$ structure (Cromer & Olsen, 1959) was chosen as a trial structure primarily on the basis of the Patterson projection $P(x, z)$ and from comparison of symmetry and cell dimensions of $PuNi_3$ and YNi_3 but also with due note of the structural similarity between other yttrium and plutonium compounds. Because of prior publication, $NbBe_3$ (Sands, Zalkin & Krikorian, 1959) should probably be considered as the prototype structure.

The trial structure was refined with the least-squares refinement program of Busing, Martin & Levy (1959) which utilizes a full matrix to refine both positional parameters and temperature factors. Observed reflections were given unit weight while unobserved reflections were given a weight of one-fifth, and convergence was assumed when all parametric shifts were less than ten per cent of the computed standard deviations. A residual, $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$, of 0·077 was obtained for the ninety-six observed reflections and of 0·099 for the total of one hundred forty-eight observed and unobserved reflections. A comparison of observed and calculated structure factors for the complete set of data is shown in Table 1. The refined positional parameters in space group $R\bar{3}m$ in the hexagonal representation are included in Table 2. Isotropic temperature factors in Å^2 for the yttrium atoms in the 3(*a*) and 6(*c*) sets are respectively 0·25 ± 0·06 and 0·07 ± 0·03 and for the nickel atoms in the 3(*b*), 6(*c*), and 18(*h*) sets are 0·06 ± 0·06, 0·19 ± 0·05, and 0·19 ± 0·03. Interatomic distances are tabulated in Table 3.

It may be noted at this point that for $l=3n$ the structure factor contributions of the 3(*a*), 3(*b*), and 6(*c*) sets are independent of permutations of *h* and *k*. For $l=6n$ the value of the *z* parameter of the 18(*h*) set causes the structure factor contribution from this set also to become independent of permutations of *h* and *k*, which results in the 6*m* symmetry observed for the *hk*6 reflections. The weak intensities of the *hk*3 reflections result from a fortuitous combination of structure parameters.

Table 2. *Refined positional parameters in space group* $R\bar{3}m$ *for a group of isomorphous compounds with* AB_3 *stoichiometry*

Atom	Set	parameters	YNi_3	YCo_3	$ThFe_3$	$GdFe_3$
A	3(*a*)	$x=y=z=$	0	0	0	0
A	6(*c*)	$x=y=$	0	0	0	0
		$z=$	0·1386 ± 0·0002	0·1399 ± 0·0005	0·1414 ± 0·0009	0·142 ± 0·001
B	3(*b*)	$x=y=$	0	0	0	0
		$z=$	0·5	0·5	0·5	0·5
B	6(*c*)	$x=y=$	0	0	0	0
		$z=$	0·3336 ± 0·0004	0·3328 ± 0·0008	0·331 ± 0·004	0·334 ± 0·002
B	18(*h*)	$x=-y=$	0·5019 ± 0·0009	0·509 ± 0·003	0·526 ± 0·005	0·487 ± 0·004
		$z=$	0·0816 ± 0·0002	0·0803 ± 0·0004	0·079 ± 0·002	0·082 ± 0·005

Table 3. *A comparison of interatomic distances in* AB_3 *compounds with* A *representing yttrium, thorium, or gadolinium and* B *representing nickel, cobalt, or iron*

Atom	Neighbor	No. of Neighbors	YNi_3 Distance (±0·02 Å)	YCo_3 Distance (±0·06 Å)	$ThFe_3$ Distance (±0·09 Å)	$GdFe_3$ Distance (±0·06 Å)
A(3*a*)	A(6*c*)	2	3·39	3·41	3·56	3·51
	B(6*c*)	6	2·87	2·90	2·99	2·97
	(18*h*)	12	3·19	3·18	3·27	3·26
A(6*c*)	A(3*a*)	1	3·39	3·41	3·56	3·51
	(6*c*)	3	3·18	3·18	3·25	3·20
	B(3*b*)	3	2·95	2·97	3·06	3·03
	(18*h*)	6	2·85	2·90	3·04	2·98
	(18*h*)	3	3·11	3·08	3·11	3·14
B(3*b*)	A(6*c*)	6	2·95	2·97	3·06	3·03
	B(18*h*)	6	2·54	2·61	2·81	2·51
B(6*c*)	A(3*a*)	3	2·87	2·90	2·99	2·97
	B(6*c*)	3	2·87	2·90	2·99	2·97
	(18*h*)	3	2·45	2·38	2·31	2·41
	(18*h*)	3	2·46	2·50	2·68	2·58
B(18*h*)	A(3*a*)	2	3·19	3·18	3·27	3·26
	(6*c*)	2	2·85	2·90	3·04	2·98
	(6*c*)	1	3·11	3·08	3·11	3·14
	B(3*b*)	1	2·54	2·61	2·81	2·51
	(6*c*)	1	2·45	2·38	2·31	2·41
	(6*c*)	1	2·46	2·50	2·68	2·58
	(18*h*)	2	2·46	2·37	2·18	2·38
	(18*h*)	2	2·52	2·65	3·00	2·77

YCo_3

Intermetallic compounds of cobalt are very frequently isostructural with their nickel analogs, but interesting exceptions occur with sufficient frequency that a structural investigation of YCo_3 was warranted. The procedure was essentially the same as for YNi_3, and again the initial alloy composition was near to 31 at.% yttrium. In this case the crystal which was obtained from the fragmented alloy was very nearly a rectangular prism, $\sim 0{\cdot}5 \times 0{\cdot}1 \times 0{\cdot}1$ mm, and X-ray measurements were made on the crystal in this form. The crystal symmetry was determined to be the same as that of YNi_3, and lattice parameters were determined by extrapolating values from four $h00$, $29° < \theta < 74°$, and seven $00l$, $17° < \theta < 59°$, reflections taken with Cu $K\alpha$ radiation and a Weissenberg camera. The extrapolated values for the hexagonal representation are $a_0 = 5{\cdot}020 \pm 0{\cdot}005$ and $c_0 = 24{\cdot}40 \pm 0{\cdot}03$Å while the corresponding rhombohedral parameters are $a_0 = 8{\cdot}634 \pm 0{\cdot}009$ Å and $\alpha_0 = 33{\cdot}80 \pm 0{\cdot}08°$. Intensity data were accumulated for thirty-three hhl reflections from timed exposures taken with a precession camera and Ag $K\alpha$ radiation. In this case seventeen reflections in the measurable region were unobserved. Refinement of a trial structure based on the $PuNi_3$ structure led to a residual of 0·085 for the thirty-three observed reflections and a weighted residual of 0·103 for the combination of observed and unobserved reflections. The refinement produced the positional parameters which are included in Table 2. Isotropic temperature factors, again in Å^2, for the yttrium atoms in the 3(a) and 6(c) sets are respectively $0{\cdot}01 \pm 0{\cdot}11$ and $0{\cdot}08 \pm 0{\cdot}07$ and for the nickel atoms in the 3(b), 6(c) and 18(h) are $0{\cdot}29 \pm 0{\cdot}16$, $0{\cdot}18 \pm 0{\cdot}11$, and $0{\cdot}09 \pm 0{\cdot}06$. A comparison of observed and calculated structure factors is included in Table 1; the agreement is considered adequate to verify that YCo_3 is isostructural with YNi_3 and $PuNi_3$ so no additional intensity data were measured. Interatomic distances are included in Table 3.

$ThFe_3$

Cromer & Olsen (1959) have reported the $CeNi_3$ structure to have space group symmetry $P6_3/mmc$ and to be closely related to the $PuNi_3$ structure. The two structures differ primarily in layering sequence rather than in atomic coordination. Florio, Baenziger & Rundle (1956) have examined the crystal symmetry and lattice parameters of $ThFe_3$ but did not attempt a complete structure determination because of difficulty in obtaining reliable intensity data. They suggest the probable space group as $P\bar{6}m2$ though they caution that intensity anomalies leave this equivocal. Their lattice parameters, $a = 5{\cdot}22$ and $c = 24{\cdot}96$ Å, are in close accord with the YNi_3 and YCo_3 parameters, and on this basis the present structural investigation was undertaken to see if $ThFe_3$ like $CeNi_3$ was closely related to the $PuNi_3$ structure.

For this investigation a 29 at.% thorium–71 at.% iron alloy was used as the starting material and was fragmented in the same manner as the yttrium–nickel and yttrium–cobalt alloys. A small needle-shaped crystal with approximately square cross-section, $\sim 0{\cdot}05 \times 0{\cdot}001 \times 0{\cdot}001$ mm, was selected from the fragmented material. The diffraction symmetry of this crystal was determined to be $\bar{3}m$ rather than the $6/mmm$ symmetry associated with the space group $P\bar{6}m2$. Lattice parameters of $a = 5{\cdot}18 \pm 0{\cdot}03$ and $c = 25{\cdot}2 \pm 0{\cdot}3$ Å were obtained from an $h0l$ precession pattern taken with Ag $K\alpha$ radiation and are quite comparable to the values noted above. The corresponding rhombohedral parameters are $a = 8{\cdot}98 \pm 0{\cdot}09$ Å and $\alpha = 33{\cdot}8 \pm 0{\cdot}5°$. Characteristic extinctions were the same as for YNi_3 and YCo_3.

Intensity data for $h0l$ reflections were accumulated with Ag $K\alpha$ radiation and a precession camera. Because of the small size of the crystal only twenty-four reflections were measurable even though the maximum exposure time of 216 hours was more than double that used for either YNi_3 or YCo_3. An additional sixteen reflections in the measurable region were unobserved. Again the $PuNi_3$ structure was chosen as the trial structure, and because of the limited number of reflections the temperature factors were arbitrarily set at the YCo_3 values and refinement was undertaken with positional parameters only. A residual of 0·108 was obtained for the twenty-four observed reflections and of 0·122 for the combination of observed and unobserved reflections. The refined positional parameters are included in Table 2 and interatomic distances are included in Table 3. A comparison of calculated and observed structure factors is included in Table 1 and again the agreement is adequate to verify that the crystal in the present investigation is isostructural with $PuNi_3$.

The diffraction patterns obtained by Florio, Baenziger & Rundle (1956) are still on file at this laboratory and were available to the present authors. A direct comparison of the diffraction patterns of the earlier investigation with those of the present investigation leaves no doubt that the apparent symmetry of the crystals of the two investigations is different.

It is possible that the crystal examined by Florio, Baenziger & Rundle and the crystal examined in the present investigation are representative of two phases with different stoichiometries. Alternatively, it is possible that the two crystals represent two different polymorphic forms of $ThFe_3$. However, on the basis of available data it seems most likely that the crystal examined by Florio, Baenziger & Rundle was a faulted arrangement of the $PuNi_3$ structure. If their crystal was faulted, singly or multiply, in such a way that an appreciable fraction of the crystal was rotated 60° about the c axis with respect to the remainder, this would introduce a pseudo-sixfold rotation axis and the positions of the diffraction maxima would conform to the diffraction symmetry $6/mmm$. If the ratio of faulted to unfaulted material were other than unity, intensity anomalies in symmetry-related reflections should result. Examination of the structure factors shows that reflections with $l \neq 3n$ would be most prone to exhibit these anomalies since for $l \neq 3n$ the rhombohedral structure requires that an allowed *hkl* reflection be associated with an extinct *khl* reflection. Thus in a diffraction pattern of a faulted crystal, a reflection which appears as *hkl* with $l \neq 3n$ should arise entirely from the faulted portion of the crystal while the symmetry-related *khl* reflection should arise entirely from the unfaulted portion of the crystal. The experimental diffraction patterns do show intensity anomalies in reflections with $l \neq 3n$ but not in reflections with $l = 3n$. The absence of anomalies in the $l = 3n$ reflections is explicable on the basis of the structure parameters as noted at the end of the YNi_3 section of this paper.

It should be emphasized that the postulated faulting would not affect the apparent size of the unit cell. Further, the diffraction patterns from such a faulted crystal would remain compatible with the observed extinction of *hk*0 reflections with $h-k \neq 3n$ and of *hhl* reflections with $l \neq 3n$ but would remove the rhombohedral constraint that $-h+k+l \neq 3n$ necessitates extinction. This third explanation thus appears to account adequately for both the similarities and differences between the two investigations of $ThFe_3$. Evidence for faulting in the related thorium–cobalt compound was reported by Florio, Baenziger & Rundle, and an examination of the YNi_3 structure of the present investigation with Cr $K\alpha$ radiation also indicated faulting in that higher-order reflections were split into distinguishable spots.

$GdFe_3$

In an investigation of the gadolinium–iron phase diagram, Copeland *et al.* (1962) found the phase $GdFe_3$ to exist with rhombohedral symmetry. Their lattice parameters are $a_0 = 5{\cdot}148$ and $c_0 = 24{\cdot}62$ Å for the hexagonal representation and $a_0 = 8{\cdot}728$ Å and $\alpha_0 = 34{\cdot}31°$ for the rhombohedral representation. Their data were taken from polycrystalline material on a diffractometer with a Geiger counter detector and Mo $K\alpha$ radiation. These authors were foresighted enough to have included in their report numerical values for twenty-nine measurable intensities in the region $\theta < 18°$. Because of the close correspondence between the cell dimensions, symmetry, and stoichiometry of this phase and the phases herein reported, the $GdFe_3$ intensity data were tested with a trial structure based on $PuNi_3$.

Computation by the present authors showed that with the reported lattice parameters fifty-eight possible reflections occurred in the region $\theta < 18°$. Six pairs of these reflections occurred in sufficiently close proximity that additive interference of the reflection intensities was probable. These six pairs correspond in position with six of the measured intensities. The additional twenty-three measured intensities could be assigned unambiguous indices while the remaining twenty-three reflections were not reported and were thus considered as unobserved. The trial structure was first refined with the twenty-three observed reflections which were unambiguously indexed. Corrections for multiplicity and Lorentz and polarization factors were applied. A residual of 0·104 was obtained. Additional refinement with inclusion of the twenty-three unobserved reflections produced a residual of 0·132; this latter refinement included the assumption that the limit of detection was one-half the lowest reported intensity which is also equal to the minimum reported difference between weak reflections. A comparison of observed and calculated structure factors is shown in Table 4, and observed and calculated intensities are also included in the Table because of the twelve interfering reflections. Refined structure parameters are included in Table 2 and interatomic distances in Table 3; the precision quoted for these interatomic distances includes the assumption of a precision of ±0·1% for the lattice parameters.

Table 4. *Comparison of observed and calculated structure factors and intensities for* $GdFe_3$ *with indices in the rhombohedral representation*

hkℓ	$\|F_o\|$	F_c	I_o	I_c
111	u*	-0.9	u	1.8
100	1.7	1.9	5	6.5
110	u	1.2	u	2.3
222	3.1	3.1	5	5.1
211	u	-2.2	u	5.6
221	u	1.7	u	3.0
333	i**	2.3	40	56.6
322	i	8.9		
$10\bar{1}$	7.0	10.2	54	114.6
332	7.1	7.8	35	36.2
210	2.3	-1.3	6	1.7
$11\bar{1}$	10.0	10.1	45	46.3
200	i	5.2	100	137.7
321	i	12.0		
433	u	-2.7	u	3.0
220	6.1	-5.5	15	12.0
444	11.9	11.3	18	16.4
311	6.3	-6.1	15	14.1
443	7.4	-6.6	20	15.8
432	i	3.1	10	6.2
331	i	0.3		
422	4.1	2.9	5	1.1
445	u	1.4	u	0.5
$20\bar{1}$	u	3.0	u	4.4
$2\bar{1}1$	u	-0.6	u	0.2
442	u	0.1	u	0.0
554	7.9	7.7	15	14.1
310	u	-0.2	u	0.0
543	2.1	2.4	2	2.7
320	u	0.4	u	0.1
533	u	0.7	u	0.1
421	7.0	7.3	20	21.4
$2\bar{1}\bar{1}$	10.1	9.0	20	15.6
431	8.9	8.5	30	28.0
300	u	-3.1	u	1.8
$2\bar{1}2$	u	0.7	u	0.1
553	10.5	9.1	20	15.1
411	i	10.8	30	40.9
330	i	11.1		
532	u	-4.1	u	5.6
644	13.5	12.0	30	23.9
542	5.7	-4.7	10	6.9
522	i	4.7	2	3.3
441	i	1.1		
$20\bar{2}$	14.6	16.1	30	36.8
$3\bar{1}1$	u	-0.9	u	0.2
643	u	2.1	u	1.2
$2\bar{2}1$	u	2.3	u	0.7
$30\bar{1}$	u	1.2	u	0.4
420	u	3.2	u	2.6
755	i	-7.5	15	8.0
$32\bar{1}$	i	-2.0		
633	u	2.3	u	0.6
410	u	1.1	u	0.3
776	6.5	6.7	5	5.2
430	6.6	7.2	10	11.8
531	u	1.9	u	0.9
521	6.8	6.3	10	8.8

* u – unobserved.

** i – probable interference because of close proximity.

The agreement in Table 4 is adequate to verify the structure. On this basis a comparison of the lattice parameters of Copeland *et al.* for $GdFe_3$ with those of Novy, Vickery & Kleber (1961) indicates that though the latter authors had assigned the correct symmetry their indexing of reflections must be in error. This seems likely to be also true of their interpretation of the $GdNi_3$ and $GdCo_3$ patterns and it thus appears probable that these last two compounds are also isostructural with $PuNi_3$.

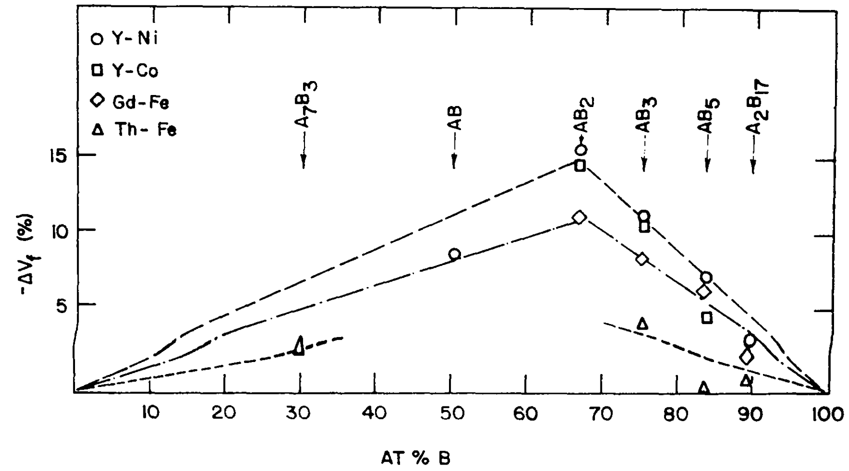

Fig. 1. Volume contractions as a function of atomic per cent for the known crystal structures in the yttrium–nickel, yttrium–cobalt, gadolinium–iron, and thorium–iron systems.

Discussion

The volume contractions associated with phase formation of the known structures in the yttrium–nickel, yttrium–cobalt, thorium–iron, and gadolinium–iron systems are shown in Fig. 1. Though these contractions are sensitive to the numerical values of the lattice parameters and the lattice parameters of the phases have not generally been measured with high precision, nonetheless there is evident an approximately linear trend between the volume of formation and atomic per cent B in the B-rich portions of each of the systems. This trend reflects the close structural relationships among these B-rich phases. Dwight (1961) has discussed the relationship between AB_2 and AB_5 structures, Florio, Baenziger & Rundle (1956) have discussed the relationship between the AB_5 and A_2B_{17} structures, and Cromer & Olsen (1959) have discussed the AB_3 structures in terms of mixed layers of AB_2 and AB_5 structures. Because of the high coordination numbers it would appear that atomic size considerations and packing efficiency are primarily responsible for the stability of these phases, and one would expect the enthalpies of phase formation to follow closely the trends exhibited by the volumes of formation (Kubaschewski & Evans, 1958).

The authors are indebted to Mr B. J. Beaudry for preparing both the yttrium–nickel and yttrium–cobalt alloys and to Dr D. T. Peterson for preparing the thorium–iron alloy. The assistance of Mr D. M. Bailey, particularly with regard to the interatomic distance program, is gratefully acknowledged. One of the authors (DAH) extends his appreciation and gratitude to the U. S. Steel Fellowship Foundation for support during the course of this investigation.

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