

order for hydrogen bond formation. This Cl-O(2') distance is shorter than the normal value of 3.2 Å and indicates that the bond is comparatively strong. The non-bonding interatomic distances less than 4 Å are Cl-C(2), 3.867 Å; Cl-C(3)', 3.837 Å; Cl-C(4'), 3.572 Å; and Cl-C(5'), 3.563 Å. The observed distances are all larger than the sum of the radii of the corresponding atoms. It is seen from Fig. 3 that the molecules are packed in such a way that the non-polar groups face each other across planes and similarly for the polar groups.

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The Crystal Structure of CeFe₇, PrFe₇, NdFe₇, and SmFe₇*

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The isostructural phases CeFe₇, PrFe₇, NdFe₇, and SmFe₇ are rhombohedral; the probable space group is $R\bar{3}m$. The lattice constants for the triply primitive hexagonal unit cells are:

	<i>a</i>	<i>c</i>	<i>c/a</i>
CeFe ₇	8.488 ± 0.003 Å	12.402 ± 0.007 Å	1.461
PrFe ₇	8.582 ± 0.003	12.462 ± 0.007	1.452
NdFe ₇	8.578 ± 0.003	12.462 ± 0.007	1.453
SmFe ₇	8.554 ± 0.003	12.441 ± 0.007	1.454

The hexagonal unit cells contain seven rare earth and forty-nine iron atoms. The atomic arrangements are intermediate between those of the $D2_d$ -CaCu₅ and Th₂Zn₁₇ structural types. A statistical occupancy of one set of positions has been proposed to account for the observed rhombohedral symmetry.

Introduction

Nassau, Cherry & Wallace (1960) have reported a phase corresponding to the formula CeFe₅ as having the $D2_d$ -CaCu₅ structure. Jepson & Duwez (1955) also reported CeFe₅ but observed that only 32 of 39 lines on their powder pattern could be accounted for by the CaCu₅ structure and that the intensity match was poor. Zarechnyuk & Kripyakevich (1963) reported the phase Ce₂Fe₁₇ ($a=8.47$, $c=12.41$ Å) to be isostructural with Th₂Zn₁₇ (Markarov & Vinogradov, 1956). Kripyakevich, Terekhova, Zarechnyuk & Burov (1963) reported

a Nd-Fe phase, in equilibrium with α -Fe, to be isostructural with Th₂Zn₁₇. Savitskii, Terekhova, Burov, Naumkin & Markova (1965) have indicated that this Nd-Fe phase corresponds to the composition Nd₂Fe₁₇ ($a=8.59$, $c=12.47$ Å). Kripyakevich & Frankevich (1966) have recently reported the phase Pr₂Fe₁₇ ($a=8.58$, $c=12.47$ Å) to have the Th₂Zn₁₇ structure.

Ray, Strnat & Feldmann (1964) have reported the preparation and magnetic properties of isostructural intermediate phases having the approximate compositions RFe₇ (R=Ce, Pr, Nd). They have shown these RFe₇ phases to form peritectically and that each represents the most iron-rich intermediate phase existing in its alloy system. The powder X-ray diffraction patterns of the RFe₇ phases have been indexed on the

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basis of hexagonal unit cells. Systematic extinctions observed on the diffraction patterns indicate rhombohedral symmetry, although an ordered rhombohedral structure is not consistent with the densities, compositions, and unit-cell volumes observed for the RFe_7 phases. Preliminary efforts to resolve the apparent structure-composition inconsistency were hampered by the lack of suitable single crystal X-ray data and reliable compositional analyses.

In the present investigation, X-ray data obtained from an untwinned $PrFe_7$ crystal plus confirmation of the compositions of the RFe_7 phases by electron microprobe analyses have been employed to determine the atomic arrangements in $PrFe_7$ and by inference the structures of $CeFe_7$, $NdFe_7$, and a phase not previously reported, $SmFe_7$.

Experimental

Electron microprobe analyses of Ce-Fe, Pr-Fe, and Nd-Fe alloys are summarized in Table 1. The analyses were performed by the Advanced Metals Research Corporation, Somerville, Massachusetts. These results confirm the compositional formula RFe_7 originally assigned to the Fe-rich phases in the Ce-Fe, Pr-Fe, and Nd-Fe alloy systems by metallographic and X-ray diffraction analyses. Chemical analyses have not been obtained for $SmFe_7$. The inclusion of $SmFe_7$ is based upon the similarity of its powder pattern to the other RFe_7 phases and upon metallographic evidence obtained from homogenized Sm-Fe alloys. A Sm-Fe alloy containing 87.5 at.% Fe was observed to be single phase after homogenization for 72 hours at 800°C.

Unit-cell constants were obtained from Debye-Scherrer powder patterns employing chromium $K\alpha$ radiation. The results for the triply primitive hexagonal unit cells of the RFe_7 phases are given in Table 2. Values for a_0 were obtained by extrapolating $hk0$ data versus the function of Nelson & Riley (1945), while c_0 values were obtained from hkl reflections with large l indices by the graphical method of successive approximations of Lipson & Wilson (1941). The powder patterns for $CeFe_7$, $PrFe_7$, $NdFe_7$, and $SmFe_7$ are given in Table 3. A double beam, recording microdensitometer was employed to obtain the line intensities. Line intensities listed for $PrFe_7$ and $NdFe_7$ were obtained by graphical integration while those for $CeFe_7$ and

Table 2. Lattice constants for the triply primitive hexagonal unit cells of the RFe_7 phases

Phase	a_0	c_0	c/a
$CeFe_7$	$8.488 \pm 3 \text{ \AA}$	$12.402 \pm 7 \text{ \AA}$	1.461
$PrFe_7$	8.582 ± 3	12.462 ± 7	1.452
$NdFe_7$	8.578 ± 3	12.462 ± 7	1.453
$SmFe_7$	8.554 ± 3	12.441 ± 7	1.454

$SmFe_7$ were approximated by multiplying the peak heights times the peak widths at half maximum.

Several fragments obtained by crushing single-phase $PrFe_7$ and $NdFe_7$ alloys were inspected to find a crystal suitable for single-crystal analyses. Invariably, these fragments were found to be twinned, and reflections having $-h+k+l=3n$ and $h-k+l=3n$ were observed simultaneously on the Weissenberg diffraction patterns. It is suspected that much of the twinning was produced by crushing the alloys. Extensive twinning was also noted in the microstructures of the annealed alloys.

A many faceted $PrFe_7$ crystal, approximating a sphere with an average diameter of 0.2 mm, was isolated from a Pr-Fe alloy containing 83 at.% Fe. Weissenberg patterns of this crystal displayed no evidence of twinning. The alloy had been previously annealed at 800°C for 40 hours, then allowed to remain in an unsealed container for several months. Immediately after annealing, the alloy was composed of $PrFe_7$ crystals in a eutectic matrix of Pr plus another Pr-Fe phase. On exposure to the atmosphere, the eutectic matrix of the alloy oxidized to a pale green powder, leaving many $PrFe_7$ crystals free of the matrix and free of mechanical distortion.

Intensity data were obtained from the $PrFe_7$ crystal by visually comparing the diffraction spots on timed Weissenberg photographs with a set of standard diffraction spots obtained from the same crystal. The intensities of 66 out of a possible 76 independent planes within the sphere of reflection for Cr $K\alpha$ radiation were observed and measured.

Structure determination

Four structural types corresponding to the composition A_2B_{17} have been reported: Th_2Ni_{17} and Th_2Fe_{17} by Florio, Baenziger & Rundle (1956) and Th_2Zn_{17} and U_2Zn_{17} by Markarov & Vinogradov (1956). All of these

Table 1. Electron microprobe analyses of rare earth-iron alloys

Alloy	Microstructure	Compositions in at. %	
		Fe	RE
Arc melted 87.5 Fe-12.5 Pr alloy used as standard.	Peritectic average center of dendrite peritectic phase	87.5 100 ± 0.5 87.6 ± 0.2	12.5 (Pr) 0.15 ± 0.03 12.4 ± 0.2
Annealed 87.5 Fe-12.5 Pr alloy.	Single phase	87.3 ± 0.2	12.7 ± 0.2 (Pr)
Annealed 87.5 Fe-12.5 Nd alloy.	Single phase	87.4 ± 0.2	12.6 ± 0.2 (Nd)
Annealed 87.5 Fe-12.5 Ce alloy.	Single phase	87.4 ± 0.2	12.6 ± 0.2 (Ce)

with those found by Vold & Peterson for the rhombohedral modification of U_2Zn_{17} . Least-squares structure refinements were employed in both of the previous investigations.

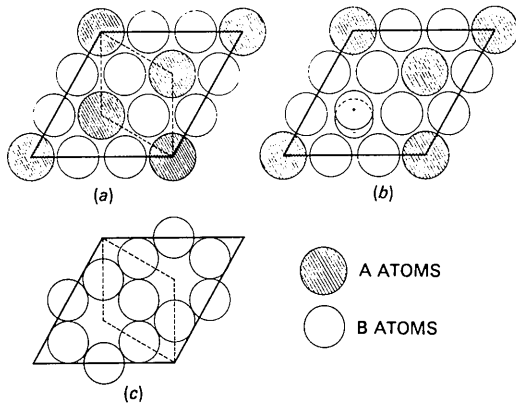


Fig. 1. Comparison of the layers in (a) $D2_a-AB_5$ and (b) A_2B_{17} structures. Alternate layers (c) are common to both types. The dashed lines in (a) and (c) indicate the unit-cell edges for AB_5 structures. The two B atoms in (b) marked + and - lie above and below and are tangent to the plane of atoms and to each other.

Table 5. Observed and calculated structure factors for $PrFe_7$, hexagonal indexing

hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c
003	11	14	048	23	23	146	9	1
006	111	107	051	10	-11	151	12	-12
009	14	19	052	10	-17	152	13	-15
011	<5	.1	054	15	-26	154	24	-24
012	<5	-1.1	055	13	-13	155	17	-15
014	25	-14	060	76	80	220	75	75
015	6	-6	063	10	-2	223	36	-33
017	22	-14	110	<5	7	226	50	52
018	<5	4	113	30	33	229	15	-17
01,10	<5	-2	116	11	-6	231	13	-17
021	20	-12	119	18	30	232	29	-13
022	12	-12	121	14	-8	234	23	-23
024	42	-32	122	12	-12	235	25	-20
025	31	-24	124	27	-23	237	11	-25
027	22	-15	125	14	-11	238	6	-7
028	<5	4	127	31	-19	241	6	-5
02,10	24	-21	128	6	-5	242	5	-5
030	54	54	131	<5	4	244	23	-21
033	68	74	132	6	4	245	29	-15
036	18	33	134	10	-7	250	10	10
039	60	62	135	<5	-5	330	36	36
041	20	15	137	13	-8	333	41	53
042	15	15	138	5	7	336	21	23
044	<5	-4	140	9	12	341	12	15
045	<5	2	143	23	31	342	14	10
047	7	7						

Table 4. Hexagonal atomic parameters in $PrFe_7$, space group $R\bar{3}m$

(i) Initial positions based on Th_2Zn_{17} . (ii) Refined positions based on Nb_2Be_{17} .

	(i)			(ii)*		
	x	y	z	x	y	z
1 Pr_I in (a) (statistically)	0	0	0	0	0	0
4 Fe_I in (c) (statistically)	0	0	0.1	0	0	0.103
6 Pr_{II} in (c)	0	0	$\frac{1}{3}$	0	0	0.340
9 Fe_{II} in (d)	$\frac{1}{2}$	0	$\frac{1}{3}$	0.500	0	0.500
18 Fe_{III} in (f)	$\frac{1}{3}$	0	0	0.297	0	0
18 Fe_{IV} in (h)	$\frac{1}{6}$	$\frac{5}{6}$	$\frac{1}{2}$	0.164	0.836	0.494

* The parameters in (ii) have been shifted by $0, 0, \frac{1}{2}$ from those originally listed for Nb_2Be_{17} (Zalkin, Sands & Krikorian, 1959).

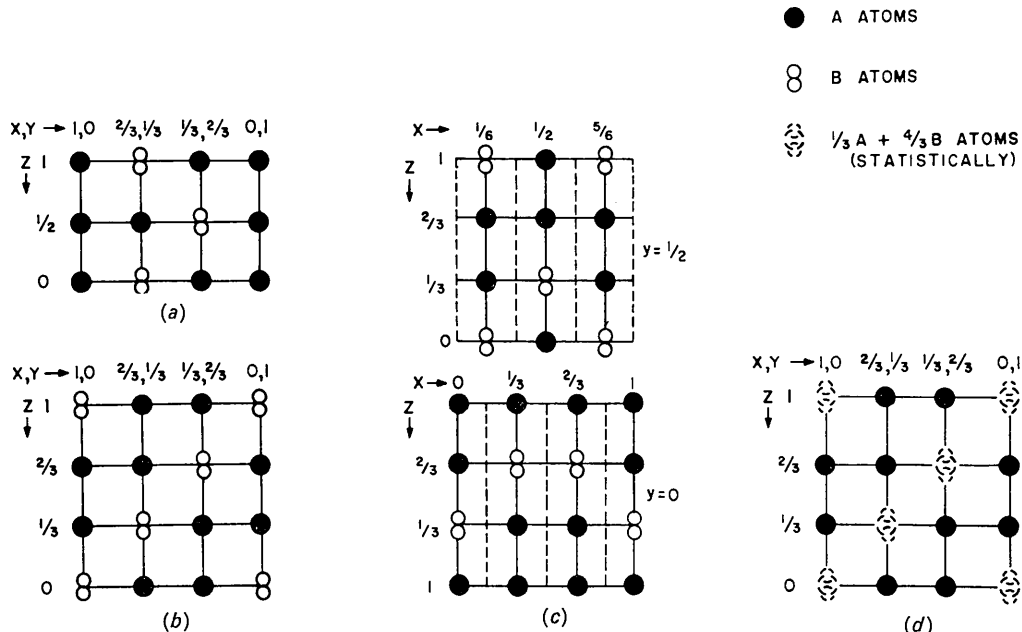


Fig. 2. Comparison of the layering arrangements in (a) Th_2Ni_{17} , (b) Th_2Zn_{17} (c) Th_2Fe_{17} , and (d) $PrFe_7$

The observed and calculated structure factors for PrFe₇ are given in Table 5. Atomic scattering factors listed in *International Tables for X-ray Crystallography* (1962) were employed for the structure factor calculations. Absorption and temperature factor corrections have been neglected. Interatomic distances based on the assumed atomic positions in PrFe₇ are given in Table 6. The only distances which appear to be abnormally short are those between the statistically occupied Pr_I and the Fe_{III} atomic positions.

Table 6. *Interatomic distances in PrFe₇*

Pr _I -2Pr _{II}	4.24	Fe _{III} -1Pr _I	2.55
6Fe _{II}	3.24	2Pr _{II}	3.03
6Fe _{III}	2.55	2Fe _I	2.85
6Fe _{IV}	3.12	2Fe _{II}	2.46
		2Fe _{III}	2.63
Pr _{II} -1Pr _I	4.24	1Fe _{III}	3.48
1Pr _{II}	3.99	2Fe _{IV}	2.59
1Fe _I	2.95	2Fe _{IV}	2.66
3Fe _{II}	3.28		
6Fe _{III}	3.03	Fe _{IV} -1Pr _I	3.12
3Fe _{IV}	3.27	1Pr _{II}	3.27
3Fe _{IV}	3.20	1Pr _{II}	3.20
3Fe _{IV}	3.10	1Pr _{II}	3.10
		1Fe _I	2.66
Fe _I -1Pr _{II}	2.95	2Fe _{II}	2.50
1Fe _I	2.57	2Fe _{III}	2.59
3Fe _{II}	2.60	2Fe _{III}	2.66
6Fe _{III}	2.85	2Fe _{IV}	2.44
3Fe _{IV}	2.66		
Fe _{II} -1Pr _I	3.24		
2Pr _{II}	3.28		
2Fe _I	2.60		
4Fe _{III}	2.46		
4Fe _{IV}	2.50		

Comparison of the powder diffraction pattern of PrFe₇ with those of NdFe₇ and SmFe₇ indicates no significant atomic shifts would be expected for these phases. The larger *c/a* ratio of CeFe₇ alters its pattern slightly and may indicate a slight adjustment of some of the atomic positions from the PrFe₇ arrangement.

Discussion

Intermediate phases which have some atomic positions statistically occupied are generally found to be stable over a range of compositions. No evidence of a solubility range near 87.5 at.% Fe has been observed in either Pr-Fe or Nd-Fe alloys homogenized for long periods between 800 and 1000°C. However, information from metallographic and X-ray diffraction studies (Ray, 1965) and from magnetic measurements (Strnat, 1965) of Ce-Fe alloys containing from 83 to 92 at.% Fe and homogenized at 837°C for 750 hours indicates

that the single-phase field in this system may extend from 84.5 to 88.5 at.% Fe. If these indications concerning Ce-Fe alloys are correct, they would account for the CeFe₅ composition (83.3 at.% Fe) reported by Jepson & Dewez (1955) and for the Ce₂Fe₁₇ composition (89.5 at.% Fe) reported by Zarechnyuk & Kripyakevich (1963). The powder diffraction patterns of the RFe₇ phases can be indexed successfully by assuming these phases to be isostructural to Th₂Zn₁₇. This appears to be the basis for the assignment of the formulas Pr₂Fe₁₇ (Kripyakevich & Frankevich, 1966) and Nd₂Fe₁₇ (Savitskii *et al.*, 1965) since no supporting analytical data are included in either paper.

Kripyakevich, Terekhova, Zarechnyuk & Burov (1963) report a Gd-Fe intermediate phase of the Th₂Zn₁₇ type to be the main component of a Gd-Fe alloy containing 86.5 at.% Fe, and a Gd-Fe intermediate phase of the Th₂Ni₁₇ type to be the main component of an alloy containing 89.5 at.% Fe. While the authors do not indicate the nature of the deviation from A₂B₁₇ stoichiometry in the Gd-Fe phase having the Th₂Zn₁₇ type structure, it appears possible that this phase may be isostructural with the RFe₇ phases reported here.

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