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Refinement of a Th_2Zn_{17} Structure: Pr_2Fe_{17}*

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The phase, previously called $PrFe_7$, has been reinvestigated by single-crystal X-ray diffraction methods using data obtained with a diffractometer and molybdenum radiation. As reported earlier, the compound is rhombohedral, space group $R\bar{3}m$, with $a=8{\cdot}585$, $c=12{\cdot}464$ Å; contrary to earlier findings, it has the composition Pr_2Fe_{17} and an ordered Th_2Zn_{17}-type structure. Ce, Nd and Sm in combination with Fe have all been reported previously to form the same structure as the Pr–Fe compound. The composition AB_7 reported for these three phases is therefore in doubt. For AB_x compounds of the $ThZn_{8.5}(Th_2Zn_{17})$ type, no conclusive crystallographic evidence has yet been put forth for x other than 8·5.

Introduction

AB_x phases with $7 \le x < 11$ have frequently been reported with x selected on the basis of metallographic evidence. When B is Be, Mg, Fe, Co, Ni or Zn and A is appropriate to the selection of B (see Table 1), phases occurring in this region often bear a resemblance to the $CaZn_5$ ($D2_d$) structure. The two most frequently encountered structure types are Th_2Ni_{17} and Th_2Zn_{17}. For the sake of simplicity, the Th_2Zn_{17} structure type is defined as comprising those compounds which are rhombohedral, have a (hexagonal) c/a ratio $\sim 1{\cdot}5$, and contain six $CaZn_5$-like subcells; the Th_2Ni_{17} structure type is defined such that it comprises the hexagonal compounds with a c/a ratio $\sim 1{\cdot}0$ and four $CaZn_5$-like subcells. This latter classification may actually encompass two or more different but closely related structures (Johnson & Smith, 1967). For the Th_2Ni_{17} type in the cerium–magnesium system, Johnson & Smith (1967) have shown that $x \sim 10{\cdot}3$. The work of Zalkin, Sands, Bedford & Krikorian (1961), Ostertag & Strnat (1966), and Cramer & Wood (1967) also indicate that Th_2Ni_{17} structures with $x > 8{\cdot}5$ are to be expected.

Table 1. *Elementary combinations found for A_2B_{17} phases*

A	*B*
Ti, Zr, Nb, Hf, Ta	Be
Sr, Ba, rare earth	Mg
Y, rare earth, actinide	Fe, Co, Ni, Zn

On the other hand, no deviation from the ideal 2:17 ratio was noted in the single-crystal work on the Th_2Zn_{17} type phases Nb_2Be_{17} (Zalkin, Sands & Krikorian, 1959) and U_2Zn_{17} (Vold & Peterson, 1961). However, Ray (1966), proposed on the basis of metallographic observations that the Th_2Zn_{17} type structures in the Ce–Fe, Pr–Fe, Nd–Fe, and Sm–Fe systems have $x=7$. He suggested that the AB_7 composition could be obtained within the limitations of the rhombohedral symmetry if one of the sixfold iron sites were occupied one-third of the time by a rare-earth atom. This model was not refined. Our first attempts to refine the structure proposed by Ray (1966) led to inconclusive results. It was apparent that the original data were of insufficient quality to show a deviation from the ordered atomic arrangement found in other Th_2Zn_{17} type phases. The data had been obtained with photographic techniques employing chromium radiation, and hence substantial absorption effects would be expected. In order to determine whether or not x deviates from 8·5, we have remeasured the intensities using single crystals selected from the original preparation, molybdenum radiation and counter techniques.

Experimental

The crystals used in this investigation were obtained from a 20 at.% Pr–80 at.% Fe sample annealed at 1000°C for 30 hours. They were magnetically removed from the oxidized matrix, and selected on the basis of their nearly spherical shape. As reported earlier, twinning is a problem although a satisfactory crystal was found which was only slightly twinned. Precession photographs established that this new crystal represented the same rhombohedral phase as the crystal used in the earlier investigation. Data obtained from a Fe $K\alpha$ ($\lambda=1{\cdot}9373$ Å) powder pattern were used in a least-squares refinement program to compute new lattice constants. For the hexagonal cell, $a=8{\cdot}585 \pm 0{\cdot}005$ Å and $c=12{\cdot}464 \pm 0{\cdot}008$ Å.

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Intensity measurements were carried out on a General Electric XRD-5 diffractometer equipped with a goniostat. The crystal closely approximated a sphere of radius 0·07 mm. The stationary-crystal stationary-counter technique (Furnas, 1957) was used; the radiation was Zr-filtered Mo $K\alpha$. Reflections from one third of the hemisphere were measured out to $2\theta \le 40°$. Corrections for a φ-dependent as well as spherical ($\mu r=2{\cdot}23$) absorption were made. Affected reflections were corrected for twinning by measuring diffractometrically the twin ratio from the intensities of the 204 (forbidden) and 024 reflections; this ratio was 0·028. Finally, the intensities, corrected for background, absorption and twinning, were averaged to give 108 independent data, which were reduced to relative $|F|$'s through the application of Lorentz–polarization factors.

Table 3. *Observed and calculated structure factors*

H	K	L	FO	/FC/	H	K	L	FO	/FC/	H	K	L	FO	/FC/	H	K	L	FO	/FC/
0	0	3	26	27	1	0	7	70	74	2	1	4	94	96	3	4	2	46	46
0	0	6	301	312	1	0	10	13	12	2	1	7	101	103	3	4	5	16	15
0	0	9	56	49	1	1	0	23	21	2	1	10	35	35	3	5	1	21	25
0	1	2	8	8	1	1	3	91	92	2	2	0	229	247	4	0	1	67	61
0	1	5	22	21	1	1	6	47	48	2	2	3	120	120	4	0	4	24	27
0	1	8	2	2	1	1	9	73	76	2	2	6	135	135	4	0	7	15	14
0	1	11	69	65	1	2	2	42	41	2	2	9	57	59	4	1	3	95	94
0	2	1	46	49	1	2	5	58	62	2	3	2	70	69	4	1	6	12	11
0	2	4	147	147	1	2	8	19	21	2	3	5	58	59	4	1	9	76	79
0	2	7	72	74	1	2	11	36	34	2	3	8	42	45	4	2	2	22	19
0	2	10	86	84	1	3	1	19	18	2	4	1	23	27	4	2	5	76	75
0	3	0	157	163	1	3	4	40	44	2	4	4	99	95	4	2	8	25	26
0	3	3	203	214	1	3	7	49	51	2	4	7	49	52	4	3	1	34	33
0	3	6	72	73	1	3	10	6	2	2	5	0	33	32	4	3	4	4	2
0	3	9	159	160	1	4	0	49	46	2	5	3	71	70	4	4	0	213	206
0	4	2	65	66	1	4	3	96	96	3	0	3	225	217	5	0	2	37	36
0	4	5	8	7	1	4	6	17	16	3	0	6	64	67	5	0	5	64	63
0	4	8	97	96	1	4	9	79	85	3	0	9	172	166	5	0	8	20	20
0	5	1	48	52	1	5	2	53	53	3	1	2	10	8	5	1	1	60	56
0	5	4	73	80	1	5	5	64	66	3	1	5	5	3	5	1	4	96	93
0	5	7	90	96	1	6	1	4	5	3	1	8	14	14	5	1	7	102	98
0	6	0	233	225	1	6	4	46	47	3	2	1	53	49	5	2	3	78	74
0	6	3	36	38	2	0	2	41	42	3	2	4	110	111	5	3	2	33	32
0	6	6	141	145	2	0	5	118	115	3	2	7	101	101	6	0	3	39	38
0	7	2	36	39	2	0	8	25	24	3	3	0	98	91	6	0	6	160	145
1	0	1	6	6	2	0	11	33	33	3	3	3	136	133	6	1	2	12	11
1	0	4	70	71	2	1	1	47	47	3	3	6	30	29	7	0	1	64	62

Determination of structure

The final parameters for Nb_2Be_{17} (Zalkin, Sands & Krikorian, 1959), shifted by $0,0,\frac{1}{2}$, were used as a starting point. Atomic scattering factors were those for the neutral atoms as listed in *International Tables for X-ray Crystallography* (1962) corrected for anomalous dispersion (Dauben & Templeton, 1955). A weighting scheme appropriate for diffractometric data (Smith, Johnson & Nordine, 1965) ($w=F_o^{1/4}, F_o<A$; $w=A^{5/4}F_o^{-1}, F_o>A$ with $A=28$) was used. Several cycles of least-squares refinement using the full-matrix program of Gantzel, Sparks & Trueblood (ACA Program no. 317, unpublished) as modified by Zalkin, Kahara, Johnson & Smith (unpublished) resulted in uniformly negative temperature factors for all atoms. A pronounced variation in the ratio of F_o/F_c as a function of F_o was observed in the direction indicative of substantial extinction effects. A secondary extinction parameter, β, of the form $F_{\text{corr}}=KF_{\text{obs}}\,[1+\beta I]$ (Zachariasen, 1963), where K is the scale factor and I is the raw intensity, was then incorporated into the refinement. The value of 8×10^{-6} was chosen for β as it gave a minimum in the conventional R index. Temperature parameters maintained their uniformity but now became all positive as a result of the correction for secondary extinction. Including all 108 data, the R value is 3·9%. Shifts in parameters for the last least-squares cycle were less than 0·001 times the estimated standard deviations. A subsequent difference Fourier synthesis showed no peak greater than 0·3 e.Å^{-3}. A conventional anisotropic temperature factor refinement did not improve the agreement; the parameters listed in Table 2 are based on the isotropic refinement. Table 3 is a list of observed and calculated structure factors. Interatomic distances are given in Table 4. The calculated density is 7·71 g.cm^{-3}, in good agreement with 7·73 ± 0·10 g.cm^{-3} previously measured (Ray, 1966).

Table 4. *Interatomic distances in* Pr_2Fe_{17}

	Ligancy	Distance	Standard deviation
Pr	6Fe(3)	3·084	0·002
	1Fe(1)	3·087	0·005
	3Fe(4)	3·111	0·002
	3Fe(4)	3·200	0·002
	3Fe(4)	3·267	0·002
	3Fe(2)	3·318	0·002
Fe(1)	1Fe(1)	2·393	0·009
	3Fe(2)	2·630	0·002
	3Fe(4)	2·635	0·003
	6Fe(3)	2·737	0·003
	1Pr	3·087	0·005
Fe(2)	4Fe(3)	2·439	0·001
	4Fe(4)	2·460	0·002
	2Fe(1)	2·630	0·002
	2Pr	3·318	0·002
Fe(3)	2Fe(2)	2·439	0·001
	2Fe(3)	2·462	0·003
	2Fe(4)	2·544	0·003
	2Fe(4)	2·674	0·003
	2Fe(1)	2·737	0·003
	2Pr	3·084	0·002
Fe(4)	2Fe(2)	2·460	0·002
	2Fe(4)	2·535	0·002
	2Fe(3)	2·544	0·003
	1Fe(1)	2·635	0·003
	2Fe(3)	2·674	0·003
	1Pr	3·111	0·002
	1Pr	3·200	0·002
	1Pr	3·267	0·002

Table 2. *Hexagonal atomic parameters for* Pr_2Fe_{17}, *space group* $R\bar{3}m$

(e.s.d.'s in parentheses)

	Wyckoff notation	$10^4 x$	$10^4 y$	$10^4 z$	B
Pr	6(*c*)	0	0	3436 (1)	0·54 (0·12) Å^2
Fe(1)	6(*c*)	0	0	960 (4)	0·55 (0·15)
Fe(2)	9(*d*)	$\frac{1}{2}$	0	$\frac{1}{2}$	0·47 (0·12)
Fe(3)	18(*f*)	2868 (3)	0	0	0·66 (0·12)
Fe(4)	18(*h*)	1696 (2)	8304	4897 (2)	0·68 (0·13)

Discussion

The crystallographic results reported here are clearly inconsistent with the conclusions based on metallographic results, X-ray powder patterns, and microprobe analyses presented in the earlier work. Ray (work in progress) has found that segregation occurs during solidification of the light rare earth–iron alloys after arc melting; consequently, the AB_7 composition determined earlier is in error. The details of this latter investigation will be presented elsewhere. Only the results and conclusions essential to explain the previous results (Ray, 1966) will be reported here.

Additional Pr–Fe alloys were prepared by arc melting. The as-melted microstructures of alloys containing 87·5 and 89·5 at.% Fe (corresponding to $PrFe_7$ and Pr_2Fe_{17}, respectively) showed that some Pr-rich eutectic had segregated to the top of the buttons in spite of precautions taken to avoid this. In the 87·5 at.% Fe alloy the amount of segregated eutectic was small, but for the 89·5 at.% Fe alloy it was larger. As a result of the segregation, the major portion of each button contained more iron than the nominal composition. After heat-treating pieces of each button to allow the peritectic reaction to go to completion, the microstructure and powder pattern of the 89·5 at.% Fe alloy showed excess iron present. On the other hand, after heat treatment the microstructure and powder pattern of a piece of the 87·5 at.% Fe alloy appeared to be single-phase. In the latter case, the segregation appears to be just sufficient to shift the major portion of the button to 89·5 at.% Fe.

The observed segregation also explains the microprobe results which apparently confirmed the earlier metallographic observations. The standard used for the microprobe analyses was an as-arc-melted Pr–Fe alloy containing nominally 87·5 at.% Fe. The microprobe results showed that the average iron content of the center of the as-cast button was the same (within ±0·2 at.%) as the iron content of annealed, single-phase Ce–Fe, Pr–Fe, and Nd–Fe alloys. The microprobe results merely reflected the accuracy of the standard alloy in which segregation to the extent noted above must have occurred.

This present crystallographic work shows that the true stoichiometry of the phase previously reported to be $PrFe_7$ is actually Pr_2Fe_{17}. Pronounced absorption effects plus the fact that no refinement was attempted of the model proposed by Ray (1966) prevented this from being discovered in the earlier work. The compositions $CeFe_7$, $PrFe_7$, and $NdFe_7$ were proposed on the basis of metallographic observations which were misleading because of segregation. Apparently, a similar type of segregation has been encountered by Buschow (1966) who reports RFe_7 phases for Ce, Pr, Nd, Sm, and Gd, and by Gebhart, Etter & Tucker (1967) who observed single-phase microstructures for a Ce–Fe alloy corresponding to $CeFe_7$.

The structure and composition found for Pr_2Fe_{17} are believed to apply also to the phases previously called $CeFe_7$, $NdFe_7$, and $SmFe_7$. The earlier microprobe results show that the iron contents of Ce–Fe, Pr–Fe, and Nd–Fe phases are identical. Powder patterns for the Ce–Fe, Pr–Fe, Nd–Fe and Sm–Fe phases are nearly identical. Buschow (1966) reports three sets of cell constants for gadolinium–iron phases in this composition range. One set is said to apply to Gd_2Fe_{17} with a Th_2Ni_{17} structure and one to Gd_2Fe_{17} with a Th_2Zn_{17} structure; slightly different values are reported for a phase to which he assigns the $PrFe_7$ structure. Since we have just shown this structure and composition to be in error, it would appear further work is necessary. A possible explanation might be found by noting that Buschow observed lines 'due to $GdFe_3$' in patterns purported to be primarily $GdFe_7$. Our experience has led us to be distrustful of apparently composite powder patterns in these systems. Too often, the similarity of cell sizes, unusual extinctions, and structures with a $CaZn_5$ type subcell have prevented us from correctly interpreting powder patterns until first elucidated by single-crystal work. Thus we feel that the unit cell reported by Buschow for $GdFe_7$ remains in doubt until corroborated by single-crystal work. Within the limits of the definition we have given to the Th_2Zn_{17} structure type, no conclusive crystallographic evidence yet exists which shows deviation from the ideal stoichiometry.

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