

SOLID-STATE PHYSICS

PrFe₅ STRUCTURE IN Pr-Fe SYSTEM

E. A. Rykova, N. A. Khatanova, and A. S. Ilyushin

The X-ray and electron diffraction studies show that following the stepwise annealing, 500 hours at 600 °C + 30 hours at 800 °C, an equilibrium Pr₂Fe₁₇ phase and the metastable phases, α-Pr and a PrFe₅ intermetallic compound of the LuMn₅ type which is a derivative of the Laves phases MgZn₂ (C14) are formed in the Pr-77 at.% Fe alloy. A scheme for rearranging PrFe₅ (CaCu₅) into PrFe₅ (LuMn₅) and PrFe₅ (AuBe₅) has been given.

We have earlier shown [1] that on the diagram of equilibrium states of Pr-Fe below 650 °C there is one two-phase region (Pr₂Fe₁₇ + α-Pr) instead of two regions reported in the literature [2]. Above 650 °C in the solid phase a two-phase region (Pr₂Fe₁₇ + PrFe₂), where the intermetallic compound PrFe₂ has the structure of Laves phases of the type MgCu₂ (C15) must be formed [2]. The attempts to detect the formation of the intermetallic compound PrFe₂ (C15) experimentally have failed and it was only synthesized upon cooling the melt at a pressure of 3200-3500 MPa [3]. The goal of the present work was to determine the structural states of the Pr-77 at.% Fe alloy at a temperature above 650 °C.

The alloy was produced in an arc furnace with a nonconsumable electrode over a copper hearth in an argon atmosphere. The alloy was prepared by using carbonyl iron and praseodymium purified by vacuum distillation, the content of impurities ranging from 10⁻⁷ to 10⁻² at.%. The stepwise annealing of the Pr-77 at.% Fe alloy (500 hours at 600 °C + 30 hours at 800 °C) was conducted in evacuated (up to high vacuum) sealed-off quartz ampules. The X-ray diffraction analysis was carried out on a DRON-1.5 diffractometer (CuK_α-radiation). The electron diffraction patterns were obtained in an electron microscope "Tesla" BS-613 at an accelerating voltage of 80 kV. The samples for electron diffraction were prepared in the form of a powder placed on a supporting copper gauze.

The electron diffraction technique has shown that in the alloy subjected to stepwise annealing several phases are formed: α-Pr, the intermetallic compounds Pr₂Fe₁₇ and PrFe₂ in two modifications of Laves phases: MgZn₂ (C14) and MgCu₂ (C15) (Fig. 1).

The results of X-ray diffraction analysis are given in Table 1, where the experimental values of interplanar spacings *d* and the observed peak intensities *I* are compared with the analogous calculated values for α-Pr [4] and for the intermetallic compounds, Pr₂Fe₁₇ [5], PrFe₂ C14 and C15 (our data).

The electron diffraction data on the phase composition of the alloy are formally confirmed by the results given in Table 1. The α-Pr phase gave peaks which correspond only to high calculated intensities, this being an indication of its small amount. In the case of the intermetallic compound Pr₂Fe₁₇ entirely all peaks were revealed. As regards the intermetallic compound PrFe₂ C14 and C15, the peaks observed corresponded to the calculated peaks only with respect to the values of *d* rather than to the intensities. Thus, according to calculations, two peaks from C14 with *d* = 2.24 and 2.43 Å must have the highest and approximately equal intensities, whereas the experimentally observed intensities of these peaks are different: the peak with *d* = 2.24 Å has the intensity higher than the peak with *d* = 2.43 Å, and no peaks with *d* = 2.63, 2.28 and 2.20 Å are observed. One peak with highest calculated intensity (*d* = 2.25 Å) which exceeds, by an order of

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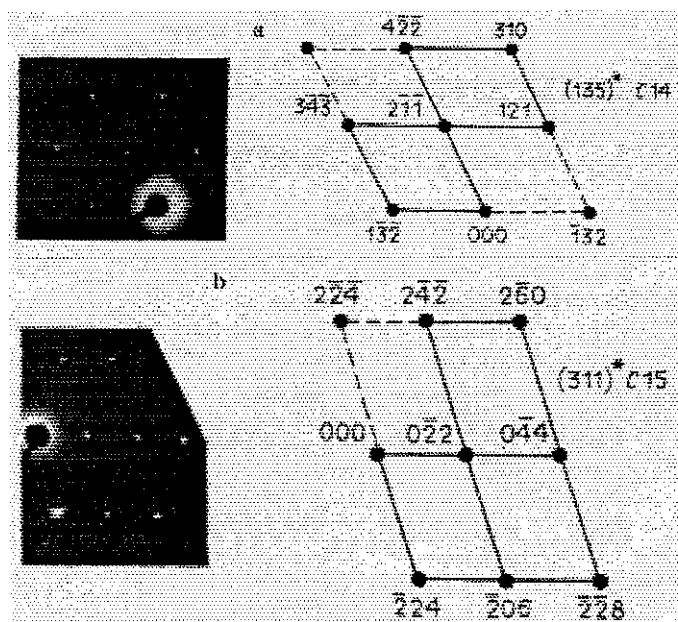


Fig. 1

Electron diffraction patterns of PrFe_2 (C14) (a) and PrFe_2 (C15) (b).

magnitude, the intensity of the most strongly pronounced peak from C14 must be observed from the C15 phase. Since the experimentally observed peak intensities with $d = 2.24 \text{ \AA}$ from C14 and $d = 2.25 \text{ \AA}$ from C15 are equal, it means that the amount of the C15 phase is small. The modifications C14 and C15 may interconvert in a displacement diffusionless way. The formation of any of the modifications in a particular alloy is determined by its stability. In the Pr-Fe alloy the stable modification is C14.

Lower values of peak intensities may be associated with the replacement of some praseodymium-atoms with large atomic amplitude by iron atoms with a smaller amplitude, which is why it has been suggested that after stepwise annealing the ordering in the lattices of PrFe_2 C14 and C15 is incomplete. The calculations of intensities were performed for two cases: for the statistical and ordered substitution of atoms. In order to calculate the peak intensities, we used the following structural data.

The structure of PrFe_2 C14 of the MgZn type has a hexagonal lattice with the parameters $a = 5.26 \text{ \AA}$, $c = 8.62 \text{ \AA}$, the space group $P6_3/mmc$ with 12 atoms in the unit cell and the following basis [6]:

$$4\text{Pr}: (1/3, 2/3, z); (2/3, 1/3, z); (1/3, 2/3, 1/2 - z); (2/3, 1/3, 1/2 + z);$$

$$2\text{Fe}: (0, 0, 0); (0, 0, 1/2);$$

$$6\text{Fe}: \pm(x, 2x, 1/4); \pm(2\bar{x}, \bar{x}, 1/4); \pm(x, \bar{x}, 1/4);$$

$$(\text{for MgZn}_2 \text{ } z = 0.062, x = -0.17).$$

The PrFe_2 C15 structure of the MgCu_2 type has a cubic lattice with the parameter $a = 7.467 \text{ \AA}$, the space group $Fd\bar{3}m$ with 24 atoms in the unit cell and the basis [6]:

$$(0, 0, 0); (1/2, 1/2, 0); (1/2, 0, 1/2); (0, 0, 1/2)$$

$$+8\text{Pr}: (000); (1/4, 1/4, 1/4)$$

$$+16\text{Fe}: (5/8, 5/8, 5/8), (5/8, 7/8, 7/8), (7/8, 5/8, 7/8), (7/8, 7/8, 5/8).$$

We first calculated the relative peak intensities on the diffraction pattern for invariable stoichiometry and statistical displacements of atoms from their sublattice into a foreign one, i.e., in calculating the structural amplitude F_{hkl} , we used the values of the atomic factors $\langle f_1 \rangle = \frac{n_{\text{Pr}} f_{\text{Pr}} + n_{\text{Fe}} f_{\text{Fe}}}{N_{\text{Pr}}}$ for the praseodymium sublattice and $\langle f_2 \rangle = \frac{n_{\text{Fe}} f_{\text{Fe}} + n_{\text{Pr}} f_{\text{Pr}}}{N_{\text{Fe}}}$, where n is the number of atoms in the sublattice and N is the number of atoms in the unit cell.

Table 1
Experimental and Calculated Values of Interplanar Spacing d
and Peak Intensity I

Experiment		Calculation									
Pr-77 at.% Fe after stepwise annealing		α -Pr		$\text{Pr}_2\text{Fe}_{17}$		PrFe_2 (C14)			PrFe_2 (C15)		
$d, \text{\AA}$	I	$d, \text{\AA}$	$I \cdot 10^{-4}$	$d, \text{\AA}$	$I \cdot 10^{-4}$	hkl	$d, \text{\AA}$	$I \cdot 10^{-4}$	hkl	$d, \text{\AA}$	$I \cdot 10^{-4}$
3.57	w	—	—	3.56	20	—	—	—	—	—	—
3.20	w	—	—	3.19	12	—	—	—	—	—	—
3.12	mw	—	—	—	—	102	3.13	80	—	—	—
2.98	w	—	—	2.98	99	—	—	—	—	—	—
2.95	vw	2.95	212	—	—	—	—	—	—	—	—
2.87	vw	—	—	2.87	27	—	—	—	—	—	—
2.81	vw	2.80	623	—	—	—	—	—	—	—	—
2.74	vw	—	—	2.74	22	—	—	—	—	—	—
—	—	—	—	—	—	110	2.63	465	220	2.64	374
2.56	w	—	—	2.56	14	—	—	—	—	—	—
2.48	w	2.47	145	2.48	102	—	—	—	—	—	—
2.43	w	—	—	—	—	103	2.43	709	—	—	—
2.39	w	—	—	2.38	77	—	—	—	—	—	—
—	—	—	—	—	—	200	2.28	108	—	—	—
2.25	m	—	—	—	—	—	—	—	311	2.25	585
2.24	m	—	—	—	—	112	2.24	732	—	—	—
—	—	—	—	—	—	201	2.20	402	—	—	—
2.14	s	—	—	2.146	173	004	2.15	59	222	2.15	92
2.13	s	—	—	2.128	261	—	—	—	—	—	—
2.09	s	—	—	2.087	50	—	—	—	—	—	—
2.08	s	—	—	2.077	86	—	—	—	—	—	—
1.90	m	—	—	1.907	60	—	—	—	—	—	—

Note: w = weak; mw = medium weak; vw = very weak; m = medium; s = strong.

Figure 2 (a and b) gives the calculated values of relative peak intensities for PrFe_2 C14 and C15 (curves 1) for the case of completely ordered structures, when all praseodymium and iron atoms occupy in their sublattices the positions in accordance with the bases of these structures, i.e., for PrFe_2 C14 in the praseodymium sublattices there are four praseodymium atoms and in the iron sublattices there are eight iron atoms; for C15 in the praseodymium sublattices there are eight praseodymium atoms and 16 iron atoms in the iron sublattices.

Curves 2 show the variations of relative intensities when in the C14 structure the praseodymium and iron sublattices each contain one foreign atom (two atoms in the C15 structure); curves 3 show that there are two foreign atoms (four atoms in the C15 structure). It can be seen that the relative intensities of the two strongly pronounced peaks decrease to a certain extent with increasing number of statistically substituted atoms. Here, the intensity of the peak with $d = 2.24 \text{ \AA}$ decreases little, whereas that of the peak with $d = 2.43 \text{ \AA}$ falls off more strongly. The situation with two peaks with $d = 2.63$ and 2.20 \AA is analogous. The peaks with low calculated intensities do not practically change. However, upon statistical substitution the intensity of the peak with $d = 2.20 \text{ \AA}$ increases, which does not agree with the experiment.

Upon ordered substitution of iron atoms for praseodymium atoms in the praseodymium sublattices, we alter the chemical composition of the compounds, thereby violating the stoichiometry: the number of praseodymium atoms in the unit cell decreases and that of iron atoms increases (Table 2).

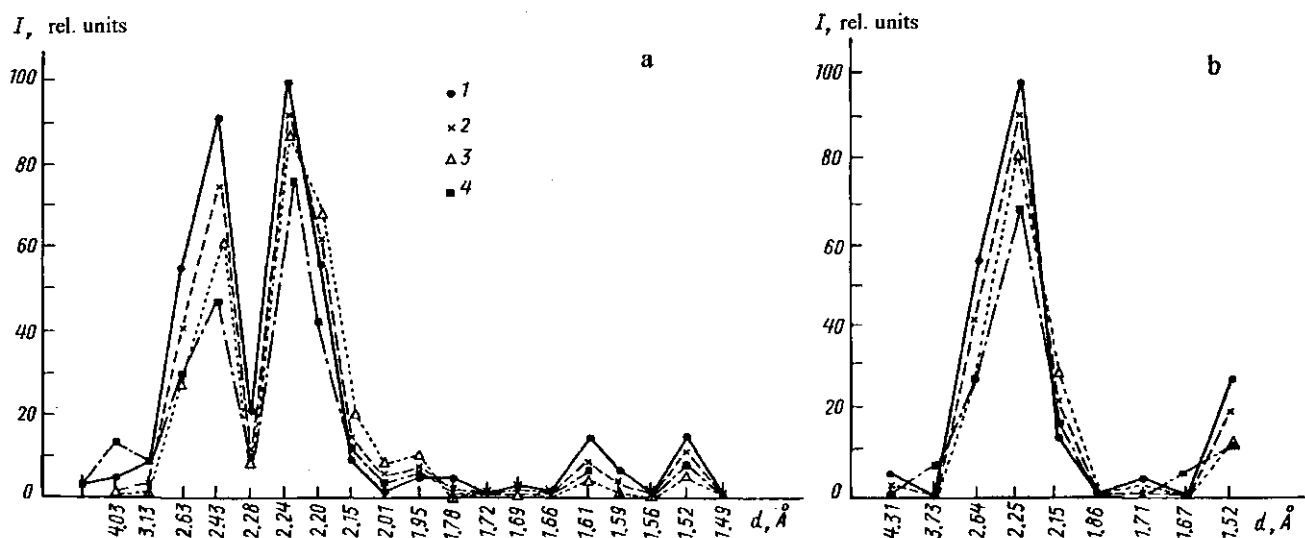


Fig. 2

Calculated values of relative peak intensities on the electron diffraction pattern of PrFe_2 C14 (a) and C15 (b) when in the praseodymium and iron sublattices there are, respectively: a—4 Pr atoms and 8 Fe atoms (4Pr/8Fe)—1; (3Pr + 1Fe)/(7Fe + 1Pr)—2; (2Pr + 2Fe)/(6Fe + 2Pr)—3; curve 4—for ordered substitution (PrFe_5 of LuMn_5 type); b—(8Pr/16Fe)—1; (6Pr + 2Fe)/(14Fe + 2Pr)—2; (4Pr + 4Fe)/(12Fe + 4Pr)—3; curve 4—for ordered substitution (PrFe_5 of AuBe_5 type).

Table 2

C14 of MgZn_2 type		C15 of MgCu_2 type	
$N_{\text{Pr}}/N_{\text{Fe}}$	Chemical composition	$N_{\text{Pr}}/N_{\text{Fe}}$	Chemical composition
4/8	PrFe_2	8/16	PrFe_2
3/9	PrFe_3	6/18	PrFe_3
2/10	PrFe_5	4/20	PrFe_5

Of all compositions listed, the PrFe_5 attracts attention, since this structure is a derivative of Laves phases [6]. The derivative of C14 of the MgZn_2 type is the PrFe_5 structure of the LuMn_5 type [7] which has the space group $C_{6v}^4 - P6_3/mmc$ (one diffraction group with $P6_3/mmc$ for MgZn_2) and the same lattice parameters as in the case of MgZn_2 with 12 atoms in the following positions [7]:

- 2Lu in (b), $z = 0.25$,
- $2\text{Mn}_{(1)}$ in (b), $z = -0.358^*$,
- $2\text{Mn}_{(2)}$ in (a), $z = 0.185$,
- $6\text{Mn}_{(3)}$ in (c), $x = 0.167$; $z = -0.047$.

In the LuMn_5 structure 8 manganese atoms are arranged in the same way as the zinc atoms in the MgZn_2 structure and the other two manganese atoms and two lutecium atoms occupy in an ordered way the magnesium positions in this structure: in the LuMn_5 structure two lutecium atoms occupy the following positions: $(1/3, 2/3, z)$ and $(2/3, 1/3, 1/2 + z)$ and two manganese atoms occupy the positions $(2/3, 1/3, z)$ and $(1/3, 2/3, 1/2 - z)$.

Since the lutecium atoms are similar in size to praseodymium atoms and the size of manganese atoms is close to that of iron atoms, in calculations of the peak intensities for PrFe_5 , we used the same values of

* An error was evidently made in [7], where the sign for $2\text{Mn}_{(1)}$ is positive.

x and z as for LuMn_5 .

Figure 2a (curve 4) shows the calculated values of relative intensities (with the diffractometer being used) for PrFe_5 of the LuMn_5 type. It can be seen that with an ordered substitution a more significant weakening of sharp peaks occurs, in which case the peak with $d = 2.43 \text{ \AA}$ also weakens. The intensity of the peak with $d = 2.20 \text{ \AA}$ also decreases in contrast to the case of statistical substitution when its intensity increases.

Since the space groups of the PrFe_2 structure of the MgZn_2 type and of PrFe_5 of the LuMn_5 type belong to the same diffraction group and their lattices have the same parameters, they cannot be distinguished by the electron diffraction method.

The group of structures of the Laves phases type also includes the type AuBe_5 [6]. The cubic unit cell of AuBe_5 (space group $T_d^2 43m$) is produced from the unit cell of MgCu_2 if in the latter the four magnesium atoms are replaced by beryllium atoms in an orderly fashion. The beryllium atoms occupy all the positions of copper atoms and half the positions of magnesium atoms in the MgCu_2 structure. The structure of the LuMn_5 type is a hexagonal analog of the structural type AuBe_5 . Figure 2b (curve 4) gives the corresponding calculated values of relative intensities for PrFe_5 of the AuBe_5 type, whence we can see that the peak with $d = 2.25 \text{ \AA}$ becomes even weaker than in the case of statistical substitution. Since the structures PrFe_2 C15 and PrFe_5 of the AuBe_5 type belong to different diffraction groups, this must give rise, in diffraction on PrFe_5 of the AuBe_5 type, to the appearance of superstructural peaks (200) with $d = 3.73 \text{ \AA}$ and (240) with $d = 1.669 \text{ \AA}$, but they were not observed because their calculated intensities were very low.

All lattices of intermetallic compounds of alloys composed of rare-earth elements and iron are derived from a hexagonal lattice of the CaCu_5 type by way of certain rearrangements of atoms and of a simultaneous displacement of the layers [8]. The CaCu_5 structure ($P6_3/mmc$) has six atoms in the unit cell and the following basis:

- 1 Ca: (000),
- 2 Cu: $(1/2, 2/3, 0)$; $(2/3, 1/3, 0)$,
- 3 Cu: $(1/2, 0, 1/2)$, $(0, 1/2, 1/2)$, $(1/2, 1/2, 1/2)$.

In the unit cell of CaCu_5 there are two types of layers. In the basal plane Ca and Cu atoms are contained, and the plane at a height of $1/2$ contains only Cu atoms.

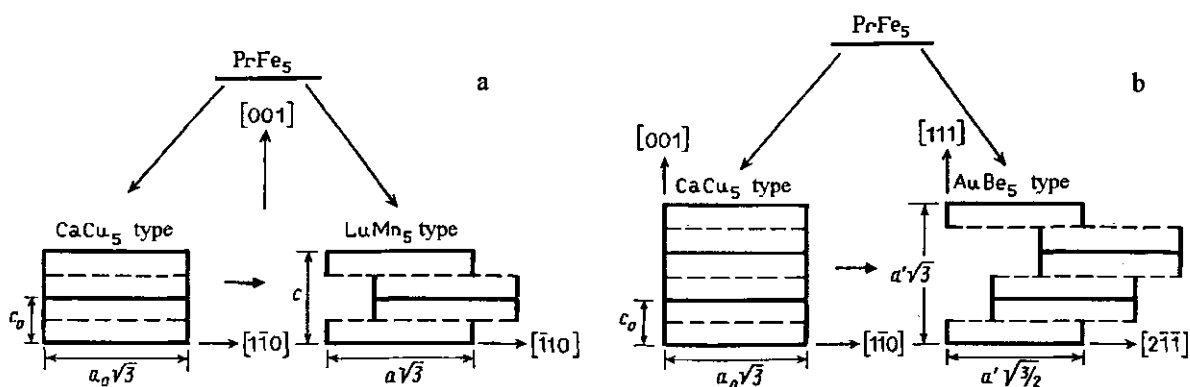
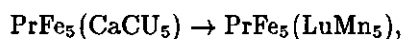
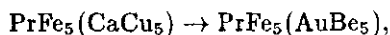


Fig. 3

Schematic diagrams of structure rearrangement from PrFe_5 of the CaCu_5 type to PrFe_5 of the LuMn_5 type (a) and to PrFe_5 of the AuBe_5 type (b). The solid lines correspond to the position of the basal plane in the CaCu_5 structure; the dashed lines correspond to its parallel plane in the same structure at a height of $(1/2)c$.

By comparing the structures PrFe_5 of the types CaCu_5 , LuMn_5 and AuBe_5 on the atomic level, we obtained the following schematic diagrams of structure rearrangements:

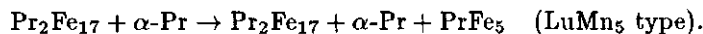




which are shown in Fig. 3.

The calculation of peak intensities in the ordered substitution of atoms and the comparison of the calculated and experimental intensities show that the stepwise annealing leads to the formation, in the Pr-77 at.% Fe alloy, of the intermetallic compound PrFe_5 , principally of the LuMn_5 type.

Thus, following the annealing, the Pr-77 at.% Fe alloy undergoes a phase transition



Here, the amount of intermetallic compound $\text{Pr}_2\text{Fe}_{17}$ decreases by a factor of about 2 after the phase transition and the remaining part, enriched with $\alpha\text{-Pr}$ atoms, is converted to PrFe_5 . The presence of more than two phases in a two-component alloy after the phase transition implies that the alloy is in a metastable state. A further prolonged annealing at 800–1000°C will be required for PrFe_5 to be enriched, due to the remaining $\alpha\text{-Pr}$, to the PrFe_2 composition, which implies the transition to an equilibrium state.

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Department of Solid-State Physics