Unusual weak increase of Curie temperature and lattice parameters in $\text{Pr}_2\text{Fe}_{16.5}\text{Zr}_{0.5}$

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Abstract. Crystal structure and magnetic and thermomagnetic properties of the $\text{Pr}_2\text{Fe}_{17-x}\text{M}_x$ compounds with $M = \text{Ti}, \text{V}, \text{Cr}, \text{Zr}, \text{Nb}$ have been studied. The change of interatomic distances is not enough to explain the growth of the Curie point and it is necessary to assume the distribution of $M = \text{Ti}, \text{V}, \text{Cr}, \text{Zr}, \text{Nb}$ atoms over the lattice positions, similar to that previously published for the $\text{Nd}_2\text{Fe}_{17-x}\text{M}_x$ compounds. It was established by neutron diffraction that \text{Zr} atoms substitute for \text{Pr} atoms in the 6\(c\) site and do not substitute for \text{Fe} atoms as might be expected from the original formula $\text{Pr}_2\text{Fe}_{16.5}\text{Zr}_{0.5}$. So, the real composition of the substituted compound studied is $\text{Pr}_{1.48(8)}\text{Zr}_{0.52(8)}\text{Fe}_{17}$. The magnetic moment of \text{Fe} atom and the magnetocaloric effect in the $\text{Pr}_2\text{Fe}_{17-x}\text{M}_x$ compounds decrease with decreasing \text{Fe} content.

1. Introduction
Magnetic refrigeration based on the magnetocaloric effect (MCE) is currently a topic of growing interest due to high efficiency, reliability, and environmental safety. A large MCE is often intrinsic to materials with large values of the magnetic moment. The best materials for the refrigeration purpose are ferromagnets or antiferromagnets. The $\text{R}_2\text{Fe}_{17}$ intermetallic compounds, where $\text{R}$ represents a rare earth element, have become promising as magnetocaloric materials due to their large magnetization, magnetic ordering temperature close to room temperature, low cost of their principal component, easy fabrication, and the absence of magnetic hysteresis. The MCE in the $\text{R}_2\text{Fe}_{17}$ binaries is moderate [1], but it can be increased by varying composition [2]. Therefore, it is interesting to study magnetic, structural and magnetothermal properties of the partial substituted $\text{Pr}_2\text{Fe}_{17-x}\text{M}_x$ compounds, $M = \text{Ti}, \text{V}, \text{Cr}, \text{Zr}, \text{Nb}$. The $\text{Pr}_2\text{Fe}_{17}$ and $\text{Nd}_2\text{Fe}_{17}$ compounds have the highest magnetic moment and unit cell volume among the $\text{R}_2\text{Fe}_{17}$ intermetallic compounds with magnetic $\text{R}$. They crystallize in the rhombohedral $\text{Th}_2\text{Zn}_{17}$-type structure in which $\text{Fe}$ atoms occupy four various positions 9\(d\), 18\(f\), 18\(h\) and 6\(c\), $\text{R}$ atoms occupy 6\(c\) position. However, the substituted alloys based on $\text{Pr}_2\text{Fe}_{17}$ are much less studied as compared to $\text{Nd}_2\text{Fe}_{17-x}\text{M}_x$ [3-5].

2. Experimental details
The $\text{Pr}_2\text{Fe}_{17-x}\text{M}_x$, $x=0, 0.5, 1$, $M=\text{Cr}, \text{V}, \text{Ti}, \text{Nb}, \text{Zr}$ compounds were prepared by induction melting. The ingots were homogenized at 1293 K for 14 days and then quenched in water. X-ray powder diffraction analysis was employed to determine the phase composition, structure type and lattice parameters under ambient conditions. A diffractometer of Empyrean Series 2 (PANalytical) and CuK\(\alpha\) radiation were used. The HighScore v.4.x programs were used for calculation of the lattice parameters.
and analysis of phase compositions. The site distribution of Zr in the Pr$_2$Fe$_{16.5}$Zr$_{0.5}$ compound was studied by means of the Fourier-diffractometer of high resolution FDHR on the fast pulse IBR-2 reactor in LNP JINR. The refinement of the structure parameters (coordinates, occupancies, unit-cell dimensions, etc.) of Pr$_2$Fe$_{16.5}$Zr$_{0.5}$ was performed using the full-profile Rietveld analysis with the “FULLPROF” program. MPMS and 7407 VSM (Lake Shore Cryotronics) devices were used for magnetic study. The saturation magnetization $M_{\text{sat}}$ at 4 K was determined by the linear extrapolation of the high-field part of the $M(H)$ curves measured on free powder samples to zero inverse internal field $(1/H)$. The temperatures of the magnetic phase transitions were determined from the ac susceptibility vs. temperature curves. The magnetization isotherms $M(H)$ were recorded on polycrystalline spherical samples in a magnetic field of strength up to 1.7 T.

3. Experimental results and discussion

3.1. Crystal structure analysis

The compounds investigated crystallize into the rhombohedral Th$_2$Zn$_{17}$-type structure. The fraction of free $\alpha$-Fe in Pr$_2$Fe$_{16.3}$M$_{0.5}$ being no larger than 3 wt.%. The Pr$_2$Fe$_{16}$M compounds contain no larger than 4 wt.% of MFe$_2$, besides Pr$_2$Fe$_{16}$Nb$_1$ with about 7 wt.% of NbFe$_2$. The solubility of M in Pr$_2$Fe$_{17}$ decreases in the following sequence as atomic radius $r$ increases: Fe ($r = 1.274$ Å), V ($1.346$ Å), Cr ($1.360$ Å), Ti ($1.462$ Å), Nb ($1.468$), Zr ($1.602$ Å). Respectively, one can see from Fig. 1 that partial substitution of Fe by larger Nb or Ti atoms leads to the maximal increase of the unit cell volume $V$. At the same time, $V$ unexpectedly decreases in the case of Cr and is almost the same with Zr, although Cr atom is larger and Zr atom is much larger than Fe atom.

![Figure 1](image-url)  
**Figure 1.** Concentration dependence of the unit-cell volume $V$ of the Pr$_2$Fe$_{17-x}$M$_x$ compounds.

3.2. Magnetic properties

The Curie temperature $T_C$ of Pr$_2$Fe$_{17-x}$M$_x$ increases for all M as is shown in Fig. 2. It is commonly assumed that $T_C$ of the rare-earth $R_2$Fe$_{17}$ compounds is determined by the competition of positive and negative exchange interactions between Fe atoms. The negative Fe-Fe exchange interaction dominates when the distance between the Fe atoms is lower than the critical one equaled to 2.45 Å. In the so-called “dumbbell” position 6c, two Fe atoms are oriented along the $c$-axis of the crystal and the Fe-Fe distance is minimal. However, $T_C$ of Pr$_2$Fe$_{16.5}$Ti$_{0.5}$ and Pr$_2$Fe$_{16.5}$Cr$_{0.5}$ are the same (Fig. 2), although their $V$ increases and decreases in comparison with $V$ for Pr$_2$Fe$_{17}$, respectively. Apparently, in this case the preferential substitution of Fe atoms by M atoms in the 6c site plays the decisive role in $T_C$ increasing, as it is in the case of the Nd$_2$Fe$_{17-x}$M$_x$ compounds [3-5].
Figure 2. Concentration dependence of the Curie temperature $T_C$ of the Pr$_2$Fe$_{17-x}$M$_x$ compounds.

The increases of the Curie temperature $\Delta T_\text{C}$ and the unit-cell volume $\Delta V$ are minimal in the case of Zr atoms ($\Delta T_\text{C} = 25$ K, $\Delta V = 0.54$ Å$^3$) in comparison with the much smaller atoms of Cr ($\Delta T_\text{C} = 49$ K, $\Delta V = -0.46$ Å$^3$), V (45 K, 1.74 Å$^3$) or Ti (49 K, 4.24 Å$^3$). Neutron diffraction was used to study this phenomenon. The results of the structural investigation of the Pr$_2$Fe$_{17}$ and Pr$_2$Fe$_{16.5}$Zr$_{0.5}$ compounds are presented in Fig. 3 and in Tables 1 and 2. It was established that Zr atoms ($r = 1.602$ Å) substitute for Pr atoms ($r = 1.828$ Å) in the 6$c$ site and do not substitute for Fe atoms as it was suggested by the original formula Pr$_2$Fe$_{16.5}$Zr$_{0.5}$ of the alloy (Table 1). So, the real composition of the studied alloy is Pr$_{1.48(8)}$Zr$_{0.52(8)}$Fe$_{17}$. The distances $D$ between neighboring Fe atoms in the Pr$_2$Fe$_{17}$ and Pr$_{1.48}$Zr$_{0.52}$Fe$_{17}$ compounds are presented in Table 2. One can see that the $D$ values are about the same in both compounds. This fact explains the almost unchanged unit-cell volume when doping Zr. As a result, the increase of $T_C$ in the Pr$_2$Fe$_{17-x}$M$_x$ system is minimal for Zr although its atomic radius is maximal among M. Our results differ from those obtained earlier for the Nd$_2$Fe$_{17-x}$Zr$_x$ system in Ref. [3], in which
neutron diffraction study showed that Zr atoms replace Fe atoms in the positions 18f (predominantly) and 6c.

**Table 1.** Structural parameters of Pr$_{2-x}$Zr$_x$Fe$_{17}$. The Th$_2$Zn$_{17}$-type structure (space group R-3m):

|     | Zr (6c) | Fe (6c) | Fe (9d) | Fe (18f) | Fe (18h) |
|-----|---------|---------|---------|----------|----------|
| x (Zr) | 0.3450(5) | 0.0968(2) | 0.1688(1) | 0.50(1) |
| z | 0.3421(5) | 0.0950(2) | 0.1694(1) | 0.68(1) |
| B, Å$^2$ | 0.81(7) | 0.50(1) | 0.50(1) |
| occ. | 2.0 | 2.0 | 2.0 |

**Table 2.** The distances D between neighboring Fe atoms in the Pr$_{2-x}$Zr$_x$Fe$_{17}$ compounds as obtained from the neutron diffraction data.

| Fe-Fe sites | 6c-6c | 6c-9d | 6c-18f | 6c-18h | 9d-18f | 9d-18h | 18f-18h | 18h-18h |
|-------------|-------|-------|--------|--------|--------|--------|---------|---------|
| D, Å (x=0)  | 2.41  | 2.63  | 2.75   | 2.64   | 2.44   | 2.46   | 2.47    | 2.54    |
| D, Å (x=0.52) | 2.37  | 2.64  | 2.75   | 2.65   | 2.44   | 2.46   | 2.49    | 2.56    | 2.67    | 2.54    |

Magnetic moment $M_{Fe}$ of a Fe atom in Pr$_2$Fe$_{17-x}$M$_x$ decreases as M content increases, for example, $M_{Fe} = 2.02$ μ$_{B}$ for $x = 0$ and $M_{Fe} = 1.69$ μ$_{B}$ for $x = 1$ in Pr$_2$Fe$_{17-x}$Ti$_x$. This effect can be explained by increase of the direct hybridization between d-electrons of Fe and M atoms.

The isothermal magnetic entropy change $\Delta S_M$ (i.e., the magnetocaloric effect MCE) was calculated from the magnetization isotherms $M(H)$ using the well-known Maxwell relation [1,2]. The MCE
decreases monotonically in the Pr$_2$Fe$_{17-x}$M$_x$ system as $x$ increases and takes about the same values for all M: -Δ$S_M$ = 2.9 J/kg*K for $x$=0 and -Δ$S_M$ = 1.9 J/kg*K for $x$=1 in a field of $\mu_0H$ = 1.7 T. Apparently, this decrease of MCE is due to the monotonic decrease of the spontaneous magnetization of the alloys during doping.

4. Conclusion
Substitution of Fe atoms in Pr$_2$Fe$_{17}$ by larger atoms M = V, Cr, Ti, Nb, Zr does not always results in a proportional increase in volume of the unit cell $V$ and Curie temperature $T_C$. Apparently, this is caused by the different character of the preferred replacement of Fe atoms by M atoms among crystallographic positions. By means of neutron diffraction, it was established that Zr atoms substitute for Pr atoms and do not substitute for Fe atoms as it was suggested by the original formula Pr$_2$Fe$_{16.5}$Zr$_{0.5}$. Therefore, the lattice parameters, interatomic distances Fe-Fe and $T_C$ of the substituted alloy change insignificantly, although the Zr atomic radius is the largest among M. The magnetic moment of the Fe atom and the magnetocaloric effect of the Pr$_2$Fe$_{17-x}$M$_x$ compounds decrease with increasing concentration of the alloying metal.

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