Structural, magnetic and magnetocaloric properties of NdPrFe\textsubscript{14}B and its hydrides

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Abstract. A systematic study of the influence of interstitial hydrogen on the structure, morphology of surface, magnetic and magnetothermal properties in multicomponent (Nd\textsubscript{0.5}Pr\textsubscript{0.5})\textsubscript{2}Fe\textsubscript{14}BH\textsubscript{x} (x = 0; 2.7; 4.3) are reported. Partial substitution of Pr for Nd allows a decrease of the spin-reorientation transition temperature from 135 K for Nd\textsubscript{2}Fe\textsubscript{14}B to 73 K for (Nd\textsubscript{0.5}Pr\textsubscript{0.5})\textsubscript{2}Fe\textsubscript{14}B. Hydrides (Nd\textsubscript{0.5}Pr\textsubscript{0.5})\textsubscript{2}Fe\textsubscript{14}BH\textsubscript{x} crystallize in a tetragonal crystal structure (space group P42/mnm) of the Nd\textsubscript{2}Fe\textsubscript{14}B-type. Both lattice constants and unit cell volume increase upon hydrogen absorption. It was also found that the surface of the hydrogenated sample was very severely damaged by the introduction of hydrogen. Magnetic studies of both initial compound and the hydrides were performed on bulk and powder samples in static and pulsed magnetic fields up to 14 and 58 T, respectively. Hydrogenation has a significant effect on magnetic properties of a multicomponent alloy (Nd\textsubscript{0.5}Pr\textsubscript{0.5})\textsubscript{2}Fe\textsubscript{14}B: Curie temperature and saturation magnetization increase, while temperature of SRT decreases (T\textsubscript{SRT} = 63 K for (Nd\textsubscript{0.5}Pr\textsubscript{0.5})\textsubscript{2}Fe\textsubscript{14}BH\textsubscript{2} with x = 2.7 and 4.3). The magnetocaloric effect (MCE) in the range of spin-reorientation transition also decreases significantly. We analyzed magnetic properties of (Nd\textsubscript{0.5}Pr\textsubscript{0.5})\textsubscript{2}Fe\textsubscript{14}BH\textsubscript{x} and compare them with that of Nd\textsubscript{2}Fe\textsubscript{14}B. Magnetic phase diagrams are constructed.

1. Introduction
In recent years, interest in multicomponent compounds (RR’\textsubscript{2})\textsubscript{2}Fe\textsubscript{14}B is quite high because the compound Nd\textsubscript{2}Fe\textsubscript{14}B has leading position among other known magnetic materials (Sm\textsubscript{2}Fe\textsubscript{17}N\textsubscript{3}, Sm\textsubscript{2}Co\textsubscript{17}, SmCo\textsubscript{5} etc.) due to its outstanding permanent-magnet properties and low cost [1, 2]. The largest hard magnetic properties of Nd\textsubscript{2}Fe\textsubscript{14}B are observed at temperatures ranging between the spontaneous spin-reorientation transition (SRT) temperature of 135 K and the Curie temperature, TC of 585 K [3, 4]. The former temperature limits the use of the Nd-Fe-B-type of magnets with
superconductors at low temperatures. Spin reorientation transition of Nd$_2$Fe$_{14}$B can be readily controlled by various substitutions both in the rare-earth and iron sublattices [5-8]. Partial substitution of Pr for Nd allows a gradually decrease of SRT temperature (from 135 K (in Nd$_2$Fe$_{14}$B) to 0 K (in Pr$_2$Fe$_{14}$B)) leading to magnets for low-temperature applications [9-12]. Such magnets can function in various environments such as liquid helium, hydrogen, nitrogen. It is not excluded that over time, light elements can penetrate into the crystal lattice of the alloy from which the magnet is prepared, changing its fundamental and functional properties. Moreover, permanent magnets based on R$_2$Fe$_{14}$B are produced with the aid of HD and HDDR-processes (hydrogenation - decomposition – desorption - recombination) [13]. Hydrogen treatment helps to increase coercivity, however, the properties of the hydrides R$_2$Fe$_{14}$BH$_x$ may drastically change with hydrogen concentration. Despite a large number of publications on the influence of hydrogen on magnetism of R$_2$Fe$_{14}$B [14, 15], only first steps in this direction are made for the substituted compounds (RR’)$_2$Fe$_{14}$B [16, 17].

The compound (Nd$_{0.5}$Pr$_{0.5}$)$_2$Fe$_{14}$B exhibits a spin-reorientation transition at 73 K (below the boiling point of liquid nitrogen) and is attractive for practice. Initial compound is studied in detail in Ref. 11. The purpose of this work is to obtain hydrides of a compound (Nd$_{0.5}$Pr$_{0.5}$)$_2$Fe$_{14}$B with different hydrogen content in different structural states (bulk and/or powder), and conduct a comprehensive study of the structure, morphology of surface, magnetic and, for the first time, magnetothermal properties in the range of «order – order» magnetic phase transition, which covers the operating interval of temperatures for this compound. Preliminary [18–21], the effect of hydrogen on the magnetic properties of Nd$_2$Fe$_{14}$B, Y$_2$Fe$_{14}$B, Lu$_2$Fe$_{14}$B single crystals was also studied.

2. Materials synthesis and experimental details

The (Nd$_{0.3}$Pr$_{0.5}$)$_2$Fe$_{14}$B alloy was obtained by a Czochralski method. The process of obtaining and certification was described in detail in our Ref. [11].

The (Nd$_{0.3}$Pr$_{0.5}$)$_2$Fe$_{14}$B sample was hydried with the special equipment [22]. Hydrogen for the hydrogenation procedure was obtained by decomposing TiH$_x$. The amount of absorbed hydrogen (Nd$_{0.3}$Pr$_{0.5}$)$_2$Fe$_{14}$BH$_x$ (x = 2.7 and 4.3 at.H/f.u.) was calculated based on the change of pressure in the reaction chamber (volumetric method). Sample (Nd$_{0.3}$Pr$_{0.5}$)$_2$Fe$_{14}$BH$_x$ with small hydrogen content x = 2.7 at.H/f.u. was obtained without destruction, while (Nd$_{0.3}$Pr$_{0.5}$)$_2$Fe$_{14}$BH$_x$ with x = 4.3 at.H/f.u. decrepitated to ultrafine powder.

The crystal structure of the hydrides was characterized by X-ray diffraction at room temperature. Microstructure was investigated by the atomic force (AFM) method on the polished surface of the specimens using a SMENA-A scanning probe microscope (Solver platform, ZAO NT-MDT, Russia) at room temperature with using standard HA_NC ETALON silicon. The obtained images were processed with Nova_1443 and Nova Px 2.0 visualization and analysis software.

The high-field magnetization measurements were performed at the Dresden High Magnetic Field Laboratory in pulsed magnetic fields up to 58 T [23]. Comparative magnetic studies of the parent compound and the hydrides were performed on free powder and bulk samples. The absolute values of magnetization were calibrated using static-field data up to 14 T. Magnetization measurements were performed using a commercial PPMS-14 magnetometer (Quantum Design, USA) between 4.2 and 650 K. To determine the magnetocaloric effect (indirect method) near magnetic phase transition, a set of magnetic isothermal M(H) curves was measured with a step of 2 K with increasing and decreasing magnetic field to 14 T. The magnetic entropy change was calculated from these magnetization isotherms by integrating the Maxwell's relation.

3. Results and discussion

(Nd$_{1-x}$Pr$_{x}$)$_2$Fe$_{14}$BH$_x$ (x = 0; 2.7; 4.3) crystallize in a tetragonal crystal structure (space group P42/mnm) of the Nd$_2$Fe$_{14}$B-type. The lattice parameters for (Nd$_{1-x}$Pr$_{x}$)$_2$Fe$_{14}$B are a=0.8816 (1) nm and c = 1.2233(3) nm, in good agreement with literature data [24]. Both lattice constants increase upon hydrogen absorption. The increase of unit cell volume is ~2.5 and ~4 % for (Nd$_{0.3}$Pr$_{0.5}$)$_2$Fe$_{14}$BH$_x$ with x = 2.7 and 4.3, respectively.
It is known [1-3] that the properties of hard magnetic materials are determined, mainly, structural state. Therefore, the study of the morphology of the material surface is extremely important, especially after a treatment. SEM studies for (Nd₀.₅Pr₀.₅)₂Fe₁₄B are described in detail in our earlier article [12]. The obtained SEM image clearly showed the grains, 50–100 µm in size.

![AFM image of the (Nd₀.₅Pr₀.₅)₂Fe₁₄B surface sample (a) and hydride surface (Nd₀.₅Pr₀.₅)₂Fe₁₄BH₂.₇ (b, c).](image)

**Figure 1.** AFM image of the (Nd₀.₅Pr₀.₅)₂Fe₁₄B surface sample (a) and hydride surface (Nd₀.₅Pr₀.₅)₂Fe₁₄BH₂.₇ (b, c).

Figure 1 shows AFM images of the surface of (Nd₀.₅Pr₀.₅)₂Fe₁₄B sample and its hydride (Nd₀.₅Pr₀.₅)₂Fe₁₄BH₂.₇. It's seen that the surface of the hydrogenated sample was very severely damaged by the introduction of hydrogen. Analysis of the surface of the hydride (Nd₀.₅Pr₀.₅)₂Fe₁₄BH₂.₇ using the AFM method (figure 1c) revealed structural elements whose dimensions are one hundred times smaller than the grain size of the initial alloy.

Figure 2a shows temperature dependence of magnetization and its derivative dM/dT (inset) for (Nd₀.₅Pr₀.₅)₂Fe₁₄BHₓ compounds (x = 0; 2.7; 3.4). It's seen that temperature of spin-reorientation transition T_SRT shifts to lower temperatures. Moreover, we found that the Curie temperature T_C, on the contrary, increases after hydrogenation (see figure 2b). Magnetic phase diagram was constructed. It was found that hydrogenation leads to the expansion of the region of uniaxial states, which is extremely important for the practical use of such materials. Figure 3 shows magnetization isotherms of (Nd₀.₅Pr₀.₅)₂Fe₁₄BHₓ (x = 0; 2.7; 4.3) measured at temperatures from 1.8 K to 270 K in static field up to 14 T (figures 3a-c) and in pulsed magnetic field up to 58 T (figure 3d). It can be seen that the saturation magnetization of the hydride is higher than that of the initial alloy.
Figure 2. Temperature dependence of magnetization (a) and magnetic phase diagram (b) of (Nd₀.₅Pr₀.₅)₂Fe₁₄BHₓ system. Inset (a): temperature dependence of the derivative dM/dT.

Figure 3. Magnetization curves of (Nd₀.₅Pr₀.₅)₂Fe₁₄BHₓ (x = 0 and 2.7) at different temperatures.

At T = 1.8 K (Nd₀.₅Pr₀.₅)₂Fe₁₄B and its hydride have an easy-cone anisotropy (there is a non-zero spontaneous magnetic moment for the field applied along the c-axis and perpendicular to the c-axis). Both compounds demonstrate a field-induced transition that disappears with increasing temperature (see, for example, the inset of figure 4e for (Nd₀.₅Pr₀.₅)₂Fe₁₄BH₂.₇).
Our next stage was the study of the magnetocaloric effect at the magnetic phase transitions. Figure 4a demonstrates MCE at spin-reorientation transitions in (Nd<sub>0.5</sub>Pr<sub>0.5</sub>)<sub>2</sub>Fe<sub>14</sub>BH<sub>x</sub> (x = 0; 2.7; 4.3).

The magnetic entropy change \(-\Delta S_M = 1.8 \text{ J/kg·K}\) at \(\Delta B = 5 \text{ T}\) for the initial sample while after hydrogenation the value of the MCE does not exceed the error of its determination. At high temperatures, the study of the magnetocaloric effect was carried out only for the initial compound (Nd<sub>0.5</sub>Pr<sub>0.5</sub>)<sub>2</sub>Fe<sub>14</sub>B. In figure 4b, these data are shown in comparison with MCE in the compound Nd<sub>2</sub>Fe<sub>14</sub>B [25]. It is seen that the kind of rare-earth ion (Nd and/or Pr) does not affect the maximum value of MCE (\(-\Delta S_M \approx 4.2 \text{ J/kg·K at } \Delta B = 1.85 \text{ T}\)).

![Figure 4](image1.png)

*Figure 4. Magnetic entropy change \(\Delta S_M\) vs. temperature (a) for (Nd<sub>0.5</sub>Pr<sub>0.5</sub>)<sub>2</sub>Fe<sub>14</sub>BH<sub>x</sub> (x = 0; 2.7; 4.3) near SR transition; (b) for (Nd<sub>0.5</sub>Pr<sub>0.5</sub>)<sub>2</sub>Fe<sub>14</sub>B and Nd<sub>2</sub>Fe<sub>14</sub>B near Curie temperature.*

![Figure 5](image2.png)

*Figure 5. (a) Magnetic entropy change \(\Delta S_M\) vs. temperature for Nd<sub>2</sub>Fe<sub>14</sub>BH<sub>x</sub> (x = 0 and 2.5) near SR transition and (b) magnetic phase diagrams of (Nd<sub>0.5</sub>Pr<sub>0.5</sub>)<sub>2</sub>Fe<sub>14</sub>BH<sub>x</sub> and Nd<sub>2</sub>Fe<sub>14</sub>BH<sub>x</sub> [26] systems.*

The maximum value of the MCE at \(T_{SRT} = 135 \text{ K}\) in Nd<sub>2</sub>Fe<sub>14</sub>B is close to that observed in (Nd<sub>0.5</sub>Pr<sub>0.5</sub>)<sub>2</sub>Fe<sub>14</sub>B at \(T_{SRT} = 73 \text{ K}\) (\(-\Delta S_M \approx 1.7-1.8 \text{ J/kg·K at } \Delta B = 5 \text{ T}\) ), however, the shape of the \(\Delta S_M(T)\) curves differ from each other. A wide maximum is observed (table-like effect) in Nd<sub>2</sub>Fe<sub>14</sub>BH<sub>x</sub> (x = 0 and 2.5).

Of particular interest was a comparison of the behavior both of the MCE value and the temperature of the SRT with respect to the hydrogen content in two systems: (Nd<sub>0.5</sub>Pr<sub>0.5</sub>)<sub>2</sub>Fe<sub>14</sub>BH<sub>x</sub> and Nd<sub>2</sub>Fe<sub>14</sub>BH<sub>x</sub>. The magnetocaloric effect (\(\Delta T_{ad}\)) for the Nd<sub>2</sub>Fe<sub>14</sub>BH<sub>x</sub> system in the SRT range was measured by the direct method in Ref. 25. It was found that with an increase in the hydrogen content in the sample from 0 to 2.5 at.H/f.u. a linear decrease in the MCE from 0.45 K to 0.33 K at \(\Delta B = 1.8 \text{ T}\) (by approx. 25%) is observed. The indirect method shows the same result (see figure 5a). Half substitution of Pr for Nd leads to decreasing of MCE almost to 0 at \(x = 2.7\) at.H/f.u. (see figure 5b). A significant
difference is demonstrated by the dependence $T_{SRT}$ (x) in (Nd$_{0.5}$Pr$_{0.5}$)$_2$Fe$_{14}$BH$_x$ and Nd$_2$Fe$_{14}$BH$_x$ systems. Numerous studies show that the Nd$_{0.5}$Fe$_{14}$BH$_x$ $T_{SRT}$ system either does not change [18, 20] or slightly increases [26, 27] at $x \leq 3.0$-3.8. A decreasing of $T_{SRT}$ is observed only at high concentrations of hydrogen. In the (Nd$_{0.5}$Pr$_{0.5}$)$_2$Fe$_{14}$BH$_x$ system, we observe a decrease in $T_{SRT}$ for compounds with $x = 2.7$ and 4.3 by the same value ($\Delta T_{SRT} = 10$ K), that leads to the expansion of the region of uniaxial states. All obtained results are significant for practice [28-30].

4. Conclusions
The hydrides (Nd$_{0.5}$Pr$_{0.5}$)$_2$Fe$_{14}$BH$_x$ (x = 2.7 and 4.3) were obtained and a systematic study of the influence of interstitial hydrogen on the structure, morphology of surface, magnetic and magnetothermal properties was carried out. Hydrogenation has a significant effect on structural and magnetic properties of a multicomponent alloy (Nd$_{0.5}$Pr$_{0.5}$)$_2$Fe$_{14}$B. Curie temperature and saturation magnetization increase, while temperature of SRT decreases. Magnetic phase diagrams are constructed. The hydrogenation leads to the expansion of the region of uniaxial states. The magnetocaloric effect in the range of spin-reorientation transition ($T_{SRT} = 63$ K) of (Nd$_{0.5}$Pr$_{0.5}$)$_2$Fe$_{14}$BH$_x$ (x = 2.7 and 4.3) hydrides diminishes significantly. Perhaps it is due to the structural state of the hydrides under study. A comparative study of MCE in the range of magnetic phase transitions for both systems Nd$_{0.5}$Fe$_{14}$BH$_x$ and (Nd$_{0.5}$Pr$_{0.5}$)$_2$Fe$_{14}$BH$_x$ was carried out. General regularities (values of MCE) and at the same time significant differences in the behavior of the $\Delta S_m(x)$, $\Delta S_m(T)$ and $T_{SRT}(x)$ dependences are revealed. These results will be useful in the practical application of materials based on the studied compounds and their hydrides.

Acknowledgment
This work is performed with financial support of the grant of Russian Science Foundation (project №18-13-00135). We acknowledge the support of HLD at HZDR (member of the European Magnetic Field Laboratory) and the Materials Growth and Measurement Laboratory (https://mgml.eu). G.P. thanks the Ministry of Science and Education of the Russian Federation, project no. 075-00746-19-00. AVA and EAT-C thank project 19-00925S of the Czech Science Foundation.

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