NANOPOWDERS OF $R_2Fe_{14}B$-TYPE COMPOUNDS IN HIGH MAGNETIC FIELDS: THE EFFECTS OF SUBSTITUTIONAL AND INTERSTITIAL ATOMS ON INTER-SUBLATTICE EXCHANGE INTERACTION

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Abstract

The fundamental magnetic characteristics of $R_2Fe_{14}B$ intermetallics are highly sensitive to atomic substitutions and interstitial absorption of light elements. In this work, both were combined, and the influence of the substitutions in the R-sublattice and hydrogen absorption on the magnetization of $(RR')_2Fe_{14}BH_x$ (R is Tm or Er, and R' is Nd) in magnetic fields up to 58T was studied. $(Tm_{0.5}Nd_{0.5})_2Fe_{14}B$ and $(Er_{0.5}Nd_{0.5})_2Fe_{14}B$ were prepared. By using direct hydrogen absorption, $(R_{0.5}Nd_{0.5})_2Fe_{14}BH_x$ compounds were obtained with hydrogen content $0 \leq x \leq 5.5$. Magnetic measurements of both the parent alloys and their hydrides were carried out on nanopowders. The strength of the inter-sublattice coupling in $(Tm_{0.5}Nd_{0.5})_2Fe_{14}B$, $(Er_{0.5}Nd_{0.5})_2Fe_{14}B$ and their hydrides is estimated by analysing high-field magnetization data. Itis shown that hydrogenation weakens the inter-sublattice exchange interaction up to 45 %. $(Tm_{0.5}Nd_{0.5})_2Fe_{14}B$, with the maximum hydrogen content of 5.5 at.H/f.u., reaches the field-induced ferromagnetic state at about 55 T.

Keywords: Rare earth, intermetallic, powder metallurgy, magnetism in solids, hydride

1. INTRODUCTION

The magnetism of rare-earth (R)-iron intermetallic compounds is very important due to the large application potential of these materials. Compounds $R_2Fe_{14}B$ are used to prepare high-performance permanent magnets[1–5]. It is well known that the R and Fe moments are ordered ferro- or ferrimagnetically depending on the rare earth[6]. The magnetic moment of light *Rs* is rather small (~3 μ_B/atom for Nd) but is parallel to the magnetic moment of Fe. It is for this reason that light rare-earth-iron intermetallics are mainly used as materials for permanent magnets [7]. The magnetic moment of heavy *Rs* is larger (10, 10, 9 and 7 μ_B/atom for Dy, Ho, Er and Tm, respectively), but it aligns antiparallel to the Fe magnetic moment. The magnetic behaviour of heavy *R* (or a mixture of heavy and light *Rs*) intermetallics with Fe is more interesting because various field-induced transitions can be expected in sufficiently external magnetic fields. The complete magnetization process ending with a field-induced ferromagnetic state often requires fields as high as tens or hundreds of Tesla [8].

Fundamental magnetic characteristics such as Curie temperature (T_C) and magnetic anisotropy of $R_2Fe_{14}B$ are highly sensitive to both atomic substitutions and absorption of light elements, e.g., hydrogen, which can be readily absorbed by the materials [9]. Hydrogen decrepitation (HD) and hydrogen disproportionation, desorption and recombination (HDDR) are two processes employed in the production of the permanent magnet [10]. Hydrogenation is beneficial not only to T_C (increasing it dramatically) in $R_2Fe_{14}B$ but also to the experiment on the magnetization study itself. Hydrogenation usually decreases the inter-sublattice R-Fe exchange and thus lowers the transition fields [11]. Besides, it is advantageous to perform experiments on the Tm-containing compounds since thulium has a Landé factor closest to unity and it needs the smallest magnetic field to reach the field-induced ferromagnetic state [8,12].

The strength of the R-Fe exchange coupling can be determined experimentally by several methods (neutron scattering, Mossbauer spectroscopy, by analysing the Curie temperatures, etc.). When single crystals are available, this coupling can be derived by analysing high-field magnetization measured along the main crystallographic directions. Hydrides are usually powdered for such studies; here, the high-field free-powder method can be employed[13].

This work presents the unique results of the investigation of magnetization processes in multicomponent compounds $(Tm_{0.5}Nd_{0.5})_2Fe_{14}B$, $(Er_{0.5}Nd_{0.5})_2Fe_{14}B$ and their hydrides with different hydrogen contents in a wide temperature range and, most importantly, using high magnetic fields. Equally important is the fact that hydrogen can occupy different lattice sites in the tetragonal $Nd_2Fe_{14}B$ crystal structure[14]. In this respect, the studies of magnetic properties of compounds with different hydrogen contents and, therefore, with different lattice sites occupied by hydrogen are of special interest. For the materials under study, the inter-sublattice coupling strength was estimated, which cannot be done using weak (up to 14T) magnetic fields.

1. EXPERIMENTAL

Single crystals of the parent $(Tm_{0.5}Nd_{0.5})_2Fe_{14}B$ and $(Er_{0.5}Nd_{0.5})_2Fe_{14}B$ compounds were grown by a modified Czochralski method. Afterwards the hydrogenation of the materials was performed[11]. We obtained powder hydrides $(Tm_{0.5}Nd_{0.5})_2Fe_{14}BH_x$ (x=1.7; 3; 4 and 5.5) and $(Er_{0.5}Nd_{0.5})_2Fe_{14}BH_x$ (x=3; 4.5 and 5.5). The phase composition of the samples was determined by standard X-ray powder diffraction at room temperature. Analysis of the diffraction patterns was performed using a refinement package FullProf. X-ray diffraction studies indicate that the investigated alloys have a tetragonal structure of the $Nd_2Fe_{14}B$ type (space group *P42/mnm*).The amount of absorbed hydrogen was calculated from the change of pressure in the reaction chamber (volumetric method). A commercial magnetometer (Quantum Design PPMS-14) was used for magnetization measurements in steady magnetic fields up to 14 T, and at temperatures between 4.2 and 80 K. High-field magnetization measurements up to 58 T were performed using a coaxial pick-up coil system at the Dresden High Magnetic Field Laboratory. Measurements of both parent alloys and their hydrides were carried out on nanopowders (average grain diameter below 200 nm).

2. RESULTS AND DISCUSSIONS

The parent $(Tm_{0.5}Nd_{0.5})_2Fe_{14}B$ and $(Er_{0.5}Nd_{0.5})_2Fe_{14}B$ compounds have a tetragonal $Nd_2Fe_{14}B$-type crystal structure with lattice parameters a = 0.876 nm, c = 1.206 nm and a = 0.877 nm, c = 1.206 nm, respectively. **Figure 1** compares the concentration dependencies of the unit-cell volume of $(Tm_{0.5}Nd_{0.5})_2Fe_{14}BH_x$ and $Tm_2Fe_{14}BH_x$ systems (the latter is adopted from [11]). The $V(x)$ grows linearly with the hydrogen content x while the tetragonal crystal structure type remains preserved in both series. It is known [14] that hydrogen can occupy different lattice sites in the tetragonal $Nd_2Fe_{14}B$ crystal structure following a certain filling scheme. For x<1.5, the 8j positions are likely to be occupied. The filling of the other sites (16k(1), 16k(2), 4e) begins at higher hydrogen contents x>1.5, i.e., when the 8j positions are fully occupied.
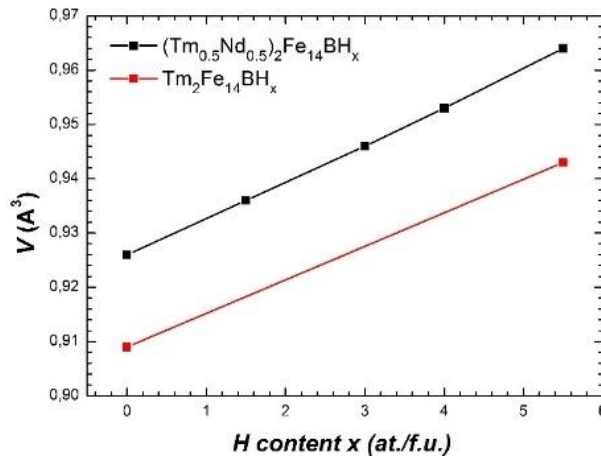
Figure 1 The unit cell volume V of $(Tm_{0.5}Nd_{0.5})_2Fe_{14}BH_x$ and $Tm_2Fe_{14}BH_x$

Figure 2 shows magnetic hysteresis loops for $(Tm_{0.5}Nd_{0.5})_2Fe_{14}B$ and $(Er_{0.5}Nd_{0.5})_2Fe_{14}B$ and their hydrides having the maximum hydrogen content of 5.5 at.H/f.u., measured in steady magnetic fields at 4.2 K. Although the hydrides demonstrate magnetization values of about 7 % higher than the parent compounds, the magnitude of the coercive field is not affected by hydrogenation.
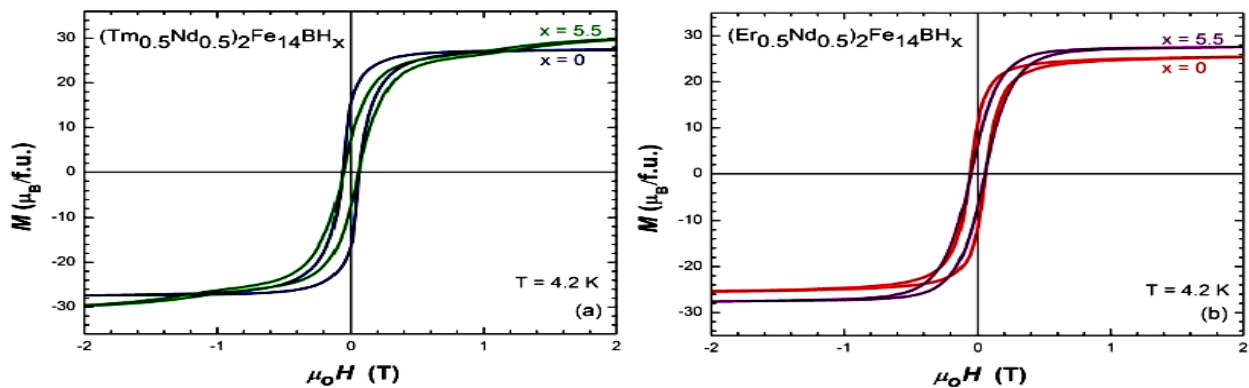

Figure 2 Magnetic hysteresis loops for $(Tm_{0.5}N_{0.5})_2Fe_{14}BH_x$ (a) and $(Er_{0.5}Nd_{0.5})_2Fe_{14}BH_x$ (b) compounds with x = 0 and 5.5 at./f.u. at 4.2 K
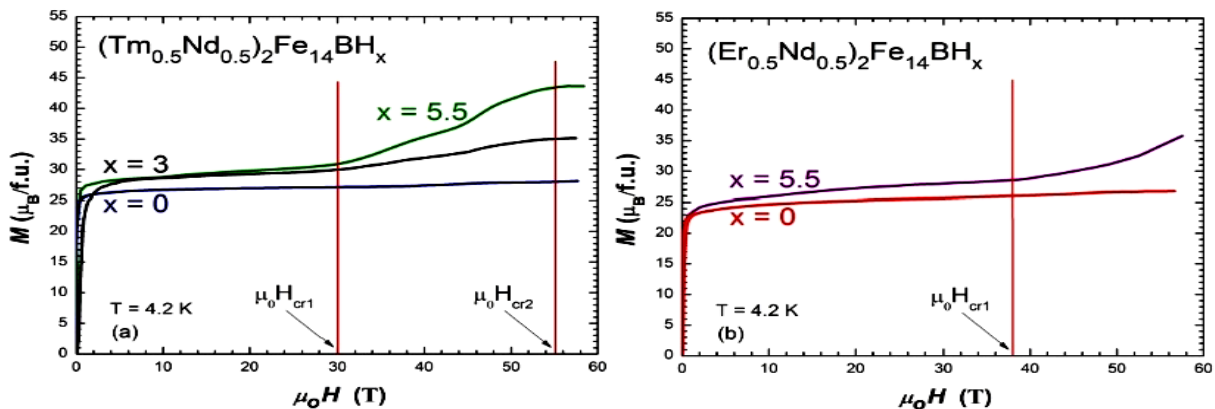
Figure 3 Field dependencies of magnetization for $(Tm_{0.5}N_{0.5})_2Fe_{14}BH_x$ (a) and $(Er_{0.5}Nd_{0.5})_2Fe_{14}BH_x$ (b) compounds with x = 0; 3 and 5.5 at./f.u. at 4.2 K.

Figure 3 shows field-dependent magnetization of the compounds $(R_{0.5}Nd_{0.5})_2Fe_{14}BH_x$ (R=Tm (a) and Er (b), x=0; 3; 5.5), measured in pulsed magnetic fields up to 58T at 4.2 K. While the parent compounds reach saturation in relatively low fields, we observe a significant growth for the hydrides at 30-40 T beyond these values. The field where the growth begins is denoted $\mu_0 H_{cr1}$ in **Figure 3**. The shape of the M(H) curves in fields exceeding $\mu_0 H_{cr1}$ is different for the Tm- and Er-containing compounds. For $(Er_{0.5}Nd_{0.5})_2Fe_{14}BH_{5.5}$, the growth is rather smooth (concave) while for $(Tm_{0.5}Nd_{0.5})_2Fe_{14}BH_3$ and $(Tm_{0.5}Nd_{0.5})_2Fe_{14}BH_{5.5}$ we observe an inflection in the M(H) curves (convex curves). For $(Tm_{0.5}Nd_{0.5})_2Fe_{14}BH_{5.5}$, with the maximum hydrogen content, the magnetization stopped increasing when the compound reached a field-induced ferromagnetic state. This occurs at the second critical transition field $\mu_0 H_{cr2}$ (also shown in **Figure 3**). **Figures 4** and **5** allow us to observe the temperature evolution of the M(H) curves for the Tm-containing hydrides $(Tm_{0.5}Nd_{0.5})_2Fe_{14}BH_3$ and $(Tm_{0.5}Nd_{0.5})_2Fe_{14}BH_{5.5}$. The M(H) curves became straight at increasing temperatures above 4.2 K.
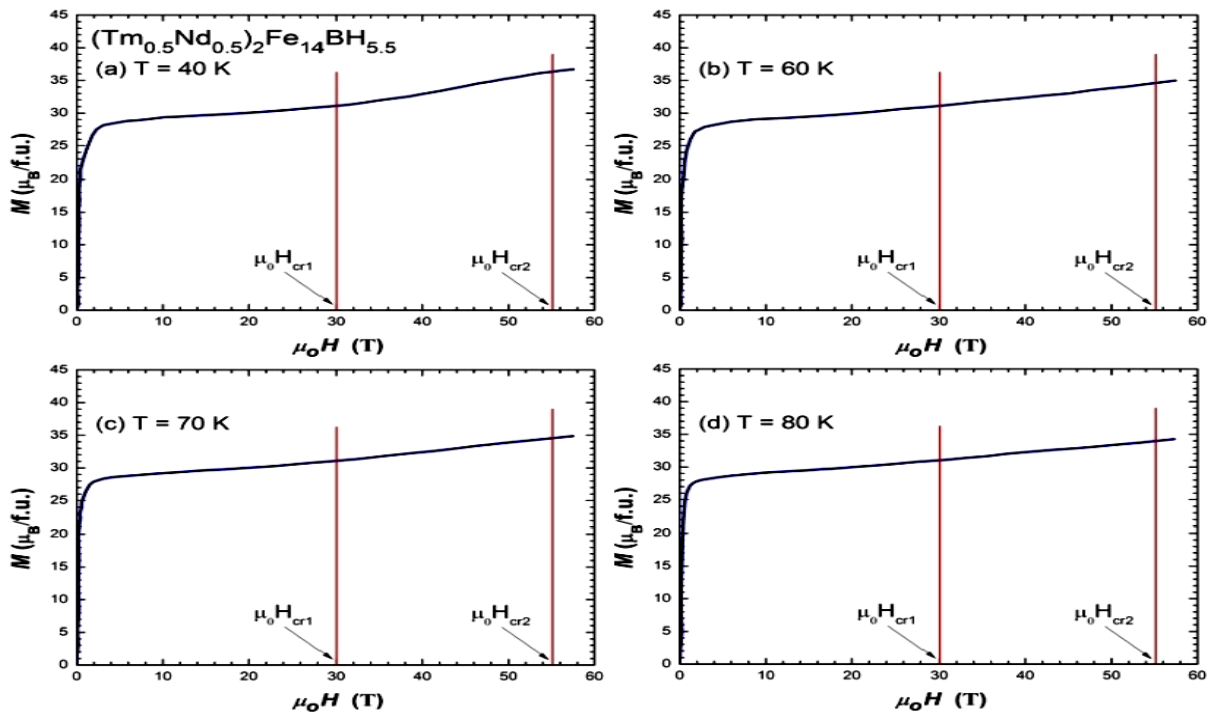
Figure 4 Field dependencies of magnetization for $(Tm_{0.5}Nd_{0.5})_2Fe_{14}BH_{5.5}$ at different temperatures:
(a) $T = 40$ K, (b) $T = 60$ K, (c) $T = 70$ K, (d) $T = 80$ K

For $R_2Fe_{14}B$-H systems, $\mu_0 H_{cr1}$ (and $\mu_0 H_{cr2}$) values allow us to estimate the parameter of the inter-sublattice exchange interaction, λ, using the following expressions[15–17]:

$$H_{cr1} = \lambda \left(M_{Fe} - 2 \cdot M_R \right) \tag{1}$$

$$H_{cr2} = \lambda \left(M_{Fe} + 2 \cdot M_R \right) \tag{2}$$

where M_{Fe} and M_R are the magnetizations of the Fe and R sublattices, respectively. The calculated values for $R_2Fe_{14}BH_x$ (R = Tm, Er, x = 0, 5.5) with the use of literature data [18, 19] are shown in **Table 1**. To evaluate the parameter λ of the inter-sublattice exchange interaction for the compound with partial substitution of Nd atoms for Tm (or Er), we used a modified expression for H_{cr1}:

$$H_{cr1} = \lambda \left(M_{Fe} - M_R \cdot \xi \right) \tag{3}$$

where $\xi = \dfrac{1}{1 + \lambda_{Nd} \cdot \chi_{Nd}}$. Here λ_{Nd} and χ_{Nd} are the exchange parameters and susceptibility of the Nd

sublattice, respectively[17]. According to our estimation, the product $\lambda_{Nd} \cdot \chi_{Nd}$ does not exceed 0.1. **Table 1** also shows data for the parent compounds and their hydrides.$\mu_0 H_{cr2}$ values were calculated using the expression:

$$H_{cr2} = \lambda \left(M_{Fe} + M_R \cdot \xi \right) \tag{4}$$
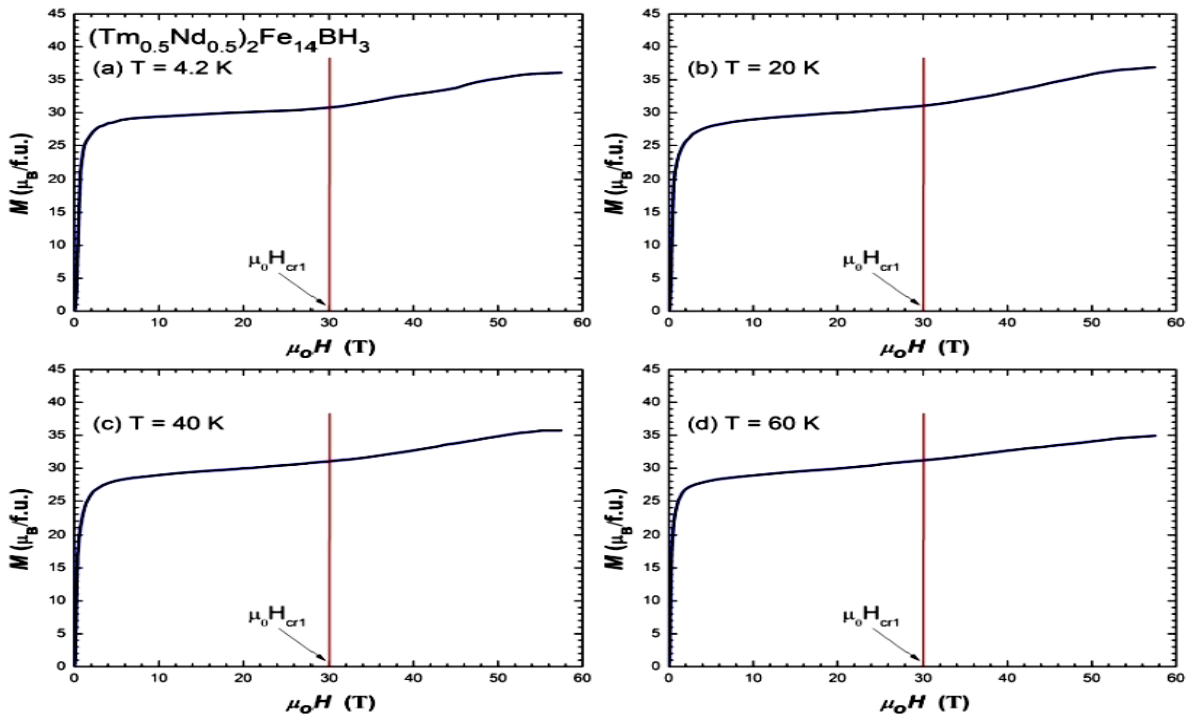
Figure 5 Field dependencies of magnetization for $(Tm_{0.5}Nd_{0.5})_2Fe_{14}BH_3$ at different temperatures: (a) T = 4.2 K, (b) T = 20 K, (c) T = 40 K, (d) T = 60 K

Table 1 Magnetic characteristics of the compounds

Compounds	M_{Fe}, μ_B	λ (T/μ_B)	$\mu_0 H_{cr1}$ (T) (exp.)	$\mu_0 H_{cr1}$ (T) (calc.)	$\mu_0 H_{cr2}$ (T) (exp.)	$\mu_0 H_{cr2}$ (T) (calc.)
$Tm_2Fe_{14}B$	31.4	2.3	40	-	95	104
$Tm_2Fe_{14}BH_{5.5}$	33.6	1.28	25	-	60	61
$Er_2Fe_{14}B$	31.4	3.3	45	-	-	163
$(Tm_{0.5}Nd_{0.5})_2Fe_{14}B$	31.4	2.3	-	58	-	87
$(Tm_{0.5}Nd_{0.5})_2Fe_{14}BH_{5.5}$	33.6	1.28	30	34	55	51
$(Er_{0.5}Nd_{0.5})_2Fe_{14}B$	31.4	3.3	-	76	-	130
$(Er_{0.5}Nd_{0.5})_2Fe_{14}BH_{5.5}$	33.6	1.65	42	-	74*	70

* Value obtained by extrapolating $M(H)$ to a field-induced ferromagnetic state

We observe a good agreement between the experimental and theoretical values of the critical transition fields for all compounds, thus validating the theoretical approach and simple mean-field model [15–17]. For $R_2Fe_{14}B$, upon the substitution of one-half of Nd atoms for Tm (or Er), the parameter λ of the inter-sublattice exchange

interaction does not change [20, 21]. For hydrides of $R_2Fe_{14}B$ and $(R_{0.5}Nd_{0.5})_2Fe_{14}B$, a significant ~45 % decrease of the parameter λ takes place.

3.   CONCLUSION

Hydrogenation is an efficient tool to tune the strength of the R-Fe exchange coupling in substituted $(R_{0.5}Nd_{0.5})_2Fe_{14}B$ (R =Er, Tm) compounds. Our results show that there is a ~ 45 % decrease in the strength of R-Fe exchange in the hydrides with maximum content hydrogen. It was found that the unit cell volume grows linearly with the hydrogen content x. The hydrogen occupation of different positions does not have a noticeable effect on the structural and magnetic properties: their change occurs smoothly. $Nd_2Fe_{14}B$ magnets with added heavy rare-earth elements when operating in an aggressive hydrogen-containing medium can change their functional properties as the absorbed hydrogen content increases. Similar studies conducted for a wide class of substituted compounds $(Nd,R)_2Fe_{14}B$ would be very important (e.g. for R = Dy).

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