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Magnetic Properties of the Intermetallic Compounds RNi (R=Gd, Tb, Dy, Sm) and Their Hydrides[1]

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Abstract—Hydrogen interaction with RNi intermetallic compounds and the influence of hydrogen on magnetic properties of these compounds were investigated. Ternary hydrides $GdNiH_{3.2}$, $TbNiH_{3.4}$, $DyNiH_{3.4}$ and $SmNiH_{3.7}$ were prepared by hydrogenation of the initial alloys at room temperature and hydrogen pressure up to 0.1 MPa. Hydrides possess orthorhombic CrB-type structure (S.G. Cmcm). The formation of hydrides results in substantial expansion of the metallic sublattices, weakening of the ferromagnetic interactions and decreasing of the paramagnetic Curie temperatures.

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INTRODUCTION

Intermetallic compounds formed between rare earths and transition metals have attracted considerable attention owing to their potential for various applications.

Influence of hydrogen on magnetic properties of materials can be caused by different factors. On the one hand, at hydrogenation the cell volume of intermetallic compounds considerably grows, distances between metal atoms increase. All types of exchange interactions, possible in R-3d compounds: an indirect exchange between rare earth ions' 4f-subshells through conduction electrons and 3d-electrons or direct exchange interaction between 3d-electrons—depend on distances between electrons and geometrical parameters of a crystal lattice. Nowadays it is not clear how lattice expansion will affect the d-d, f-d or f-f exchange interactions in the general case. Experimental investigations revealed that geometrical expansion of lattice at hydrogenation results in the strengthening of d-d exchange interaction in the intermetallic compounds with high iron content (e.g. R_2Fe_{17}, $R_2Fe_{11}Ti$): the paramagnetic Curie temperature considerably grows and the magnetic moment of Fe atoms increases [1–3]. On the contrary, in case of RFe_2 compounds the decreasing of the unit cell volume results in the increasing of the Curie temperature [4].

Electronic structure and electron density distribution can strongly depend on the hydrogen atoms' charge state. The charge state change also can lead to the change of magnetic properties at hydrogenation. Electron density at Fermi level is one of the major factors determining magnetism. Redistribution of electron density in a conduction 3d-band at hydrogenation results in electron density redistribution at Fermi level [5, 6]. Thus, hydrogenation of intermetallic compounds can be considered as rather powerful method for magnetic properties modification of already known materials or new compounds.

The data available in the literature concerning the interaction of some RNi IMC with hydrogen are insufficient. The hydrogen interaction with LaNi, YbNi, LuNi, ErNi, PrNi and CeNi intermetallic compounds have been already investigated earlier [7–10]. It is known that RNi compounds interact with hydrogen at rather soft conditions (low hydrogen pressure and room temperature) and absorb about 3 hydrogen atoms per formula unit. Hydrides of LaNi, CeNi and PrNi retain the structure of the intermetallic compounds (structure type CrB, S.G. Cmcm). Introduction of hydrogen atoms leads to cell volumes increase in this case. IMC with FeB-type structure (S.G. Pnma) undergo structural transition during the hydrogenation, their hydrides also possess CrB-type structure [7–11].

Intermetallic compounds RNi (R = Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm) are ferromagnetic materials with Curie temperatures below liquid-nitrogen temperature. The effective magnetic moments of these compounds are close to the magnetic moment values of the free lanthanide ions. The magnetization magnitude of SmNi in paramagnetic region was too small to estimate correctly the effective moment and paramagnetic Curie temperature values [12]. Besides, it is known that GdNi, HoNi, ErNi and DyNi have large values of the MCE near the transition temperature [5, 6]. Magnetic properties of RNi hydrides (R–Gd, Tb, Dy, Sm) were not investigated earlier.

Thus, the basic purpose of the given work was the research of hydrogenation process of the RNi compounds and magnetic properties of these IMC and ternary hydrides.

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[1] The article was translated by the author.

Table 1. Lattice parameters of the IMC RNi and ternary hydrides

Composition	Structure type	Lattice parameters, Å	Z	V, Å^3	$\Delta V/V$, %
GdNi	CrB	$a = 3.778(4)$, $b = 10.337(6)$, $c = 4.238(5)$	4	165.54(3)	–
$GdNiH_{3.2}$	CrB	$a = 3.767(2)$, $b = 11.576(7)$, $c = 4.733(3)$	4	206.45(2)	24.7
TbNi	TbNi (low-temperature modification)	$a = 21.31(2)$, $b = 4.211(4)$, $c = 5.454(2)$, $\beta = 97.43°$	12	485.48(4)	–
$TbNiH_{3.4}$	CrB	$a = 3.742(2)$, $b = 11.516(6)$, $c = 4.707(3)$	4	202.88(2)	25.4
DyNi	FeB	$a = 7.025(4)$, $b = 4.181(3)$, $c = 5.445(2)$	4	159.94(2)	–
$DyNiH_{3.4}$	CrB	$a = 3.759(2)$, $b = 11.368(4)$, $c = 4.655(2)$	4	199.00(2)	24.4
SmNi	CrB	$a = 3.782(3)$, $b = 10.375(4)$, $c = 4.301(2)$	4	168.76(3)	–
$SmNiH_{3.7}$	CrB	$a = 3.791(2)$, $b = 11.644(4)$, $c = 4.761(2)$	4	210.15(2)	24.5

EXPERIMENTAL

The present work represents the hydrogenation process study of GdNi (CrB-type structure), DyNi (FeB-type), TbNi (TbNi-type structure, low-temperature modification) and SmNi (CrB-type). Also the magnetic properties study for these compounds and their hydrides has been carried out.

The starting intermetallic compounds RNi were synthesized by arc melting under argon atmosphere in a furnace with a non-consumable tungsten electrode and water-cooled copper tray. Nickel (purity of 99.99%) and rare earth metals (99.9%) were used as a starting components and titanium sponge as a getter. The starting amounts of rare-earths were corrected due to waste of metal during the melting process. To ensure homogeneity, the samples were turned and remelted several times.

Hydrogen sorption properties were investigated on a Sievert type volumetric apparatus at room temperature and hydrogen pressures up to 1 MPa. The composition of the hydrides was calculated from volumetric measurements using Van der Vaals equation.

X-ray powder diffraction measurements for starting alloys and hydrides were performed to establish the phase composition of the samples and calculate the lattice parameters. The characteristic X-ray used was CuK_α.

RNi alloys easily interact with hydrogen at room temperature and hydrogen pressure about 0.1 MPa. Ternary hydrides possess orthorhombic CrB-type structure. In case of GdNi and SmNi introduction of hydrogen atoms leads to expansion of the unit cells without structure transformation. In case of TbNi and DyNi the ternary hydrides formation is accompanied by metal sublattice structure transformation (FeB–CrB structure transition). These results agree with the available literature data about ternary hydrides of other RNi compounds [7–11]. Lattice parameters of ternary hydrides are summarized in Table 1.

The unit cell volume increase in all cases exceeds ~24% (the given values were calculated considering the different number of formula units per unit cell).

Magnetization measurements were performed at vibration magnetometer in temperature range 78–300 K. Tablet-shaped samples (150–400 mg) were used in these experiments.

RESULTS AND DISCUSSION

The transition temperatures of the RNi intermetallic compounds and ternary hydrides appeared to be lower than liquid-nitrogen temperature (78 K). Therefore we focused on the analysis of the paramagnetic region. Calculated temperature dependences of reciprocal susceptibilities are linear in temperature range 78–300 K and follow the Curie-Weiss law $\chi = C/(T–\theta)$ in all cases except SmNi and $SmNiH_{3.7}$ samples. That allowes to estimate the values of paramagnetic Curie temperature θ_p and effective magnetic moment μ_{eff}.

Magnetic moment – field (M–H) isotherms are linear in the temperature range 78–300 K both for DyNi and its hydride (Fig. 1). It means, that they are paramagnetic at temperatures above 78 K. Temperature dependences of a magnetic moment (M) and reciprocal susceptibility ($1/\chi$) for DyNi and $DyNiH_{3.4}$ are represented at Fig. 2. On the basis of reciprocal susceptibility temperature dependences the paramagnetic Curie temperature values (θ_p) and the magnetic moment per formula unit were calculated using the Curie-Weiss law. For DyNi the effective magnetic moment (μ_{eff}) is found to be 10.3 μ_B and paramagnetic Curie temperature θ_p =51 K. For hydride μ_{eff}= 10.1 μ_B, e.i. the effective magnetic moment practically has not changed in comparison with initial intermetallic compound. Paramagnetic Curie temperature has fallen to θ_p = 3 K after hydrogenation.

IMC TbNi is a paramagnetic in the temperature range 78–300 K (Fig. 3). Hydride $TbNiH_{3.4}$ is a paramagnetic at

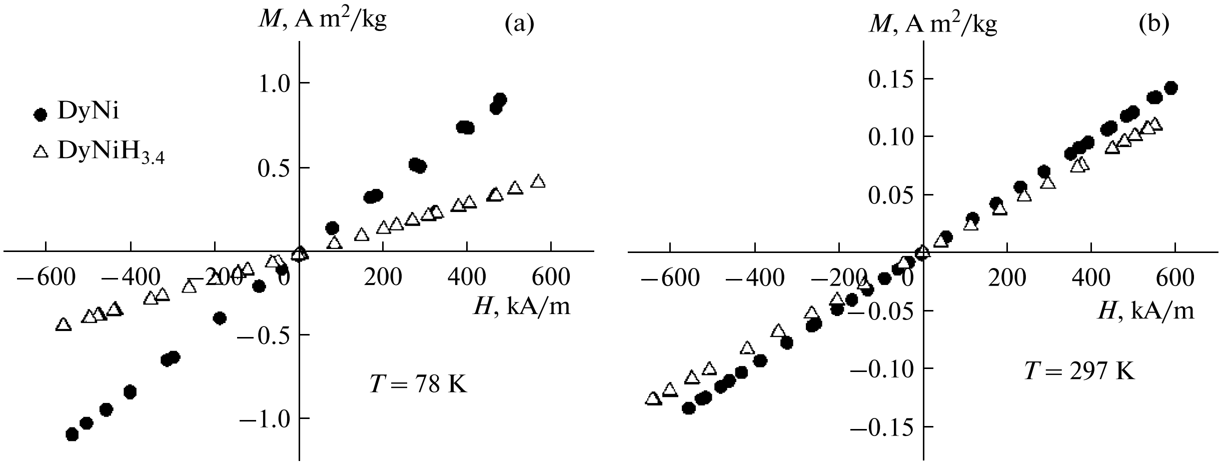

Fig. 1. Magnetization curves of the DyNi and its ternary hydride at 78 and 297 K.

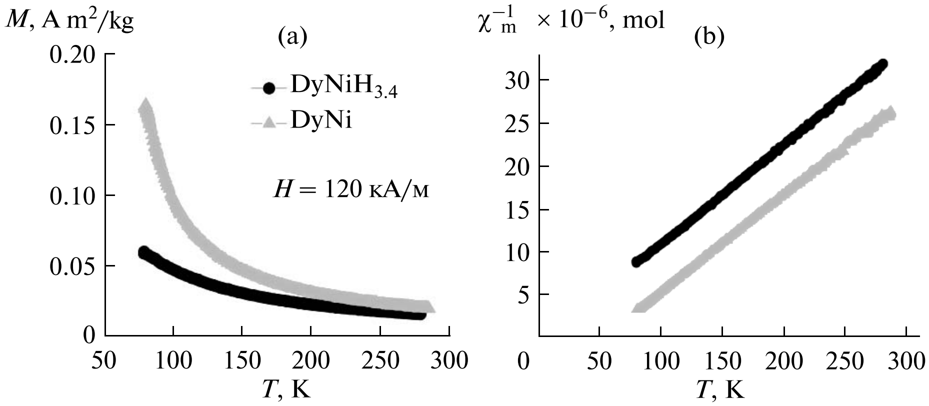

Fig. 2. Temperature dependences of the magnetic moment (M) and reciprocal susceptibility ($1/\chi$) for DyNi and $DyNiH_{3.4}$ samples.

room temperature, but at 78 K a small hysteresis in fields up to 80 kA/m is observed (Fig. 4). The small deviation of the $\chi(T)$ dependence from the Curie-Weiss law at temperatures 78–120 K indicates the presence of ferromagnetic component in ternary hydride. The reciprocal susceptibility temperature dependence of the TbNi sample follows the Curie-Weiss law down to 78 K (Fig. 5). Paramagnetic Curie temperatures θ_p and the effective magnetic moments μ_{eff} for TbNi and its hydride have been calculated: for TbNi $\mu_{eff} = 10.0\ \mu_B$, $\theta_p = 56$ K, for hydride the magnetic moment almost has not change ($\mu_{eff} = 10.3\ \mu_B$), but paramagnetic Curie temperature has strongly decreased ($\theta_p = -12$ K). This fact can indicate the presence of antiferromagnetic ordering at low temperatures.

GdNi and $GdNiH_{3.2}$ are also paramagnetic in the temperature range 78–300 K. It follows from the temperature dependences of magnetic moments and reciprocal susceptibilities (Fig. 6). Reciprocal susceptibility temperature dependences are linear and can be described by Curie-Weiss law. It allowes to calculate the effective magnetic moments values (8.3 and 7.5 μ_B for GdNi and $GdNiH_{3.2}$, accordingly) and paramagnetic Curie temperatures θ_p (80 and 21 K for GdNi and $GdNiH_{3.2}$, accordingly).

Magnetic properties of SmNi and $SmNiH_{3.7}$ differ from the above described samples. In this case magnetic moment of hydride sample is higher than the magnetic moment of IMC. Magnetic moment - field dependences of hydride sample are strongly nonlinear both at 78 K and at room temperature (Fig. 7). Reciprocal susceptibility temperature dependences of the SmNi and its ternary hydride are also non-linear and cannot be described within the Curie-Weiss law. Therefore there is no way to calculate the values of the effective magnetic moments and the paramagnetic Curie temperatures for these samples (Fig. 8). It is necessary to note, however, that the X-ray powder diffraction pattern of the $SmNiH_{3.7}$ sample revealed the presence of SmH_2 phase (Fig. 9), whereas SmNi sample did not contain any impurity phase (Fig. 10).

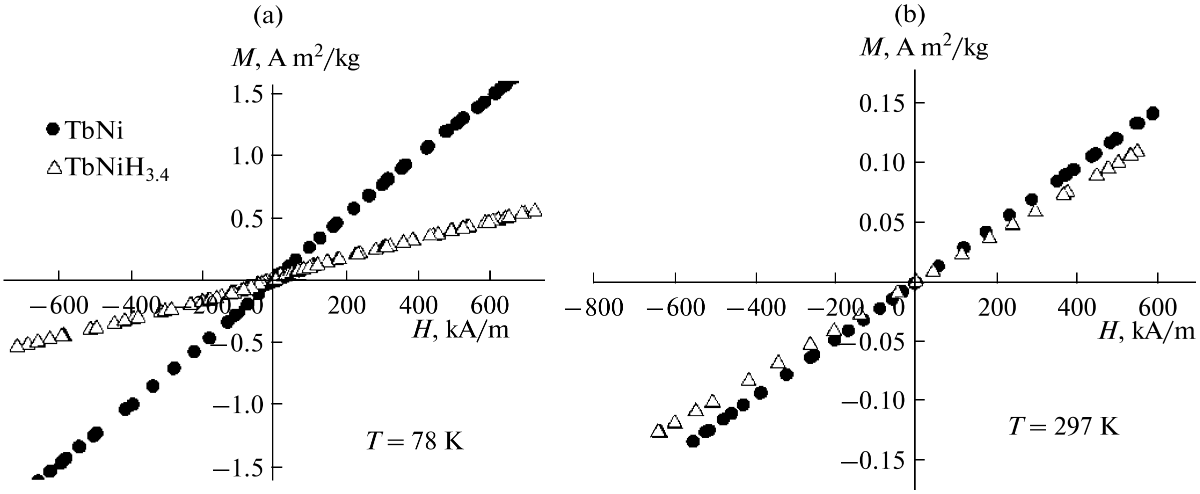

Fig. 3. Magnetization curves of the TbNi and its ternary hydride at 78 and 297 K.

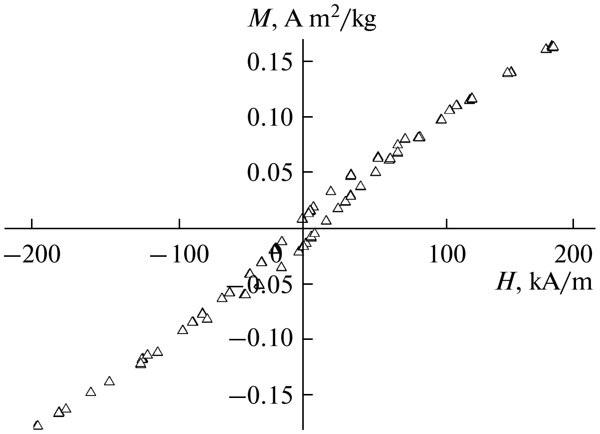

Fig. 4. Magnetization curves of the $TbNiH_{3.4}$ sample at $T = 78$K.

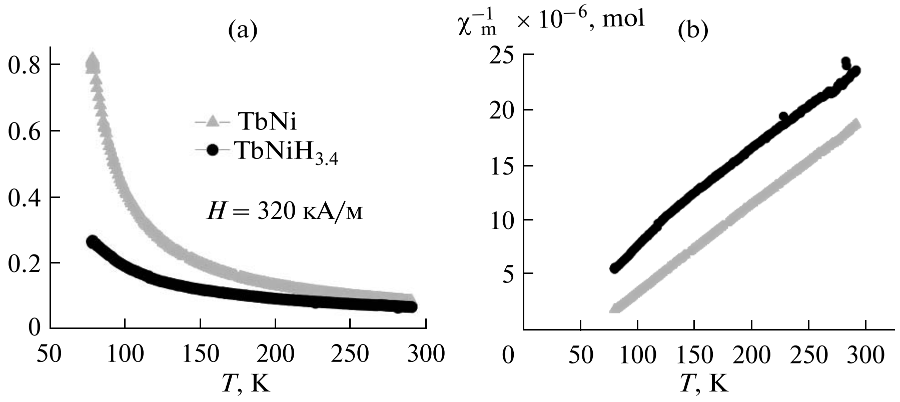

Fig. 5. Temperature dependences of the magnetic moment (*M*) and reciprocal susceptibility ($1/\chi$) for TbNi and $TbNiH_{3.4}$ samples.

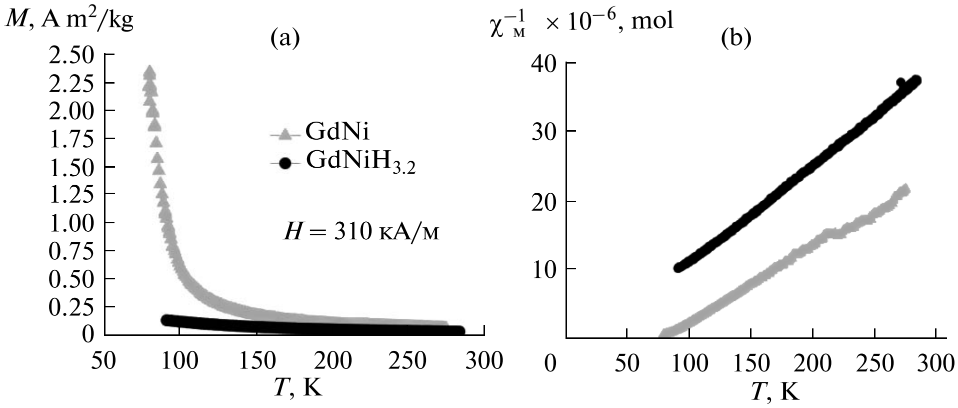

Fig. 6. Temperature dependences of the magnetic moment (M) and reciprocal susceptibility ($1/\chi$) for GdNi and GdNiH$_{3.2}$ samples.

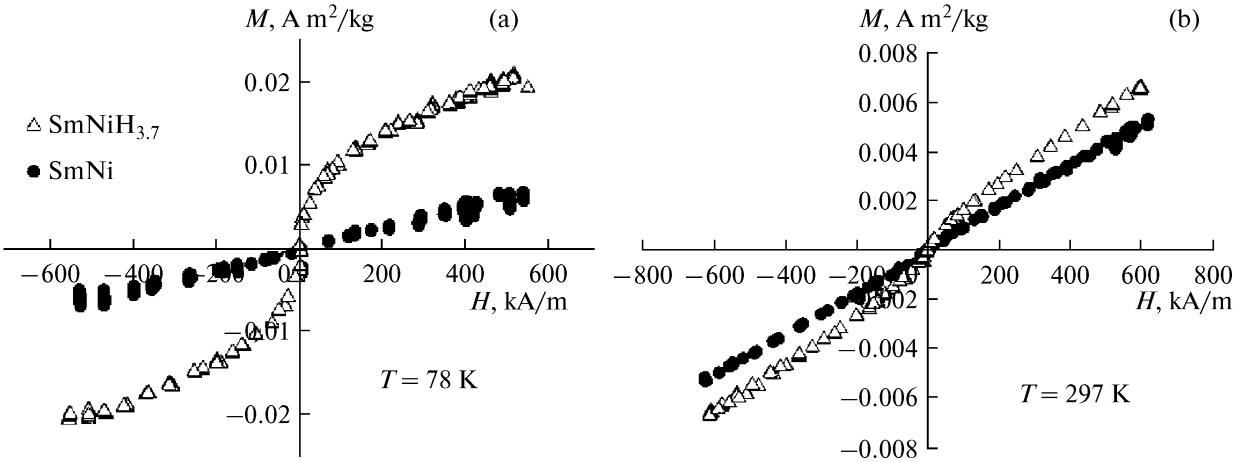

Fig. 7. Magnetization curves of the SmNi and SmNiH$_{3.7}$ samples at 78 and 297 K.

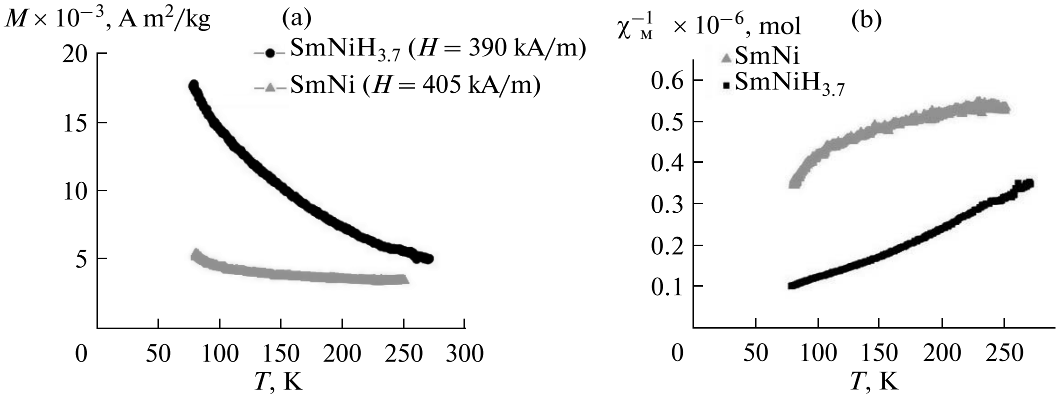

Fig. 8. Temperature dependences of the magnetic moment (M) and reciprocal susceptibility ($1/\chi$) for SmNi and SmNiH$_{3.7}$ samples.

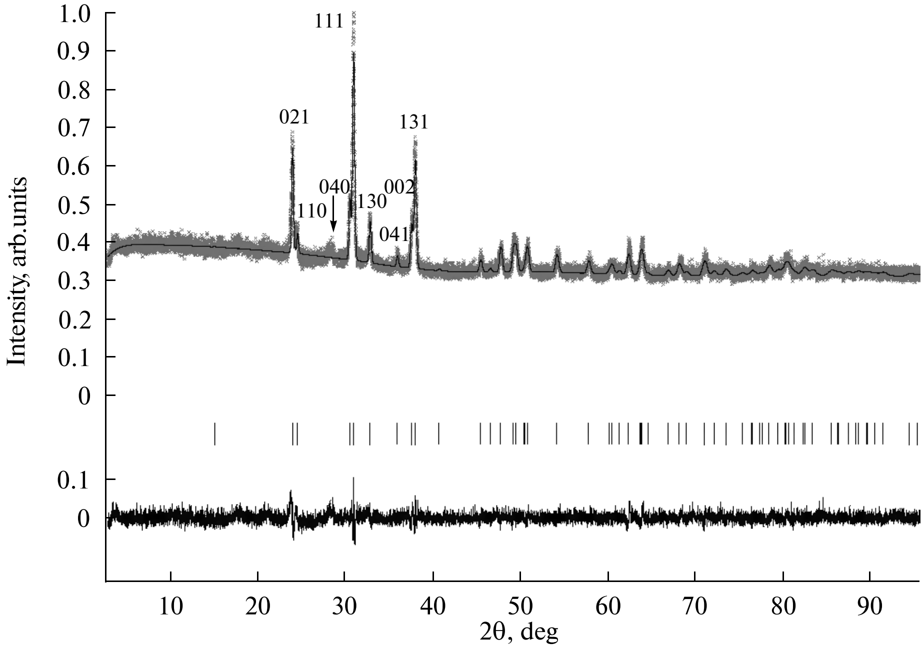

Fig. 9. X-ray powder diffraction pattern of the $SmNiH_{3.7}$ sample. The arrow indicates the reflection of impurity phase (probably SmH_2).

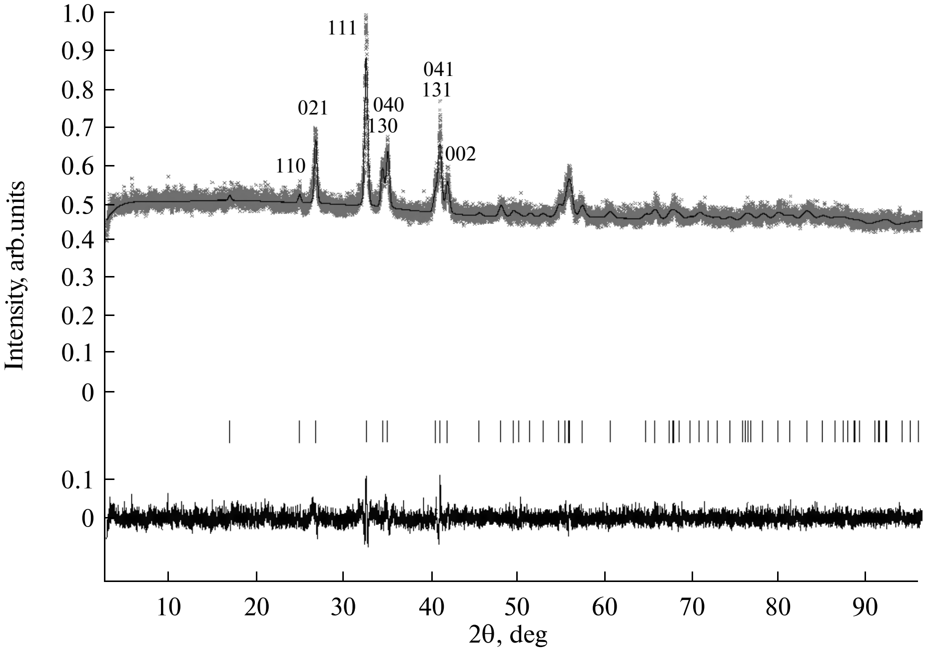

Fig. 10. X-ray powder diffraction pattern of the SmNi sample.

Table 2. Magnetic properties of the IMC RNi and ternary hydrides ($m_{eff.}$ – effective magnetic moment per REM atom, $\mu(R)$ – free Ln^{3+} ions magnetic moment)

Composition	$\mu_{eff.}$, μ_B		μ (R), μ_B	θ_p, K		T_C , K
SmNi	–	–	0.71	–	–	45 [12]
$SmNiH_{3.7}$	–	–		–	–	–
GdNi	8.3	7.8–8.1 [5,12]	7.0	80	77 [12]	69–71 [5,12]
$GdNiH_{3.2}$	7.5	–		21	–	–
TbNi	10.0	9.7 [12]	9.0	56	40 [12]	52 [12]
$TbNiH_{3.4}$	10.3	–		–12	–	–
DyNi	10.3	10.7 [12]	10.0	51	64 [12]	59–62 [6,12]
$DyNiH_{3.4}$	10.1	–		3	–	–

CONCLUSIONS

The results of the present investigation showed that hydrogenation of the RNi compounds leads to weakening of the ferromagnetic interaction and decreasing of the magnetic transition temperatures (Table 2). The paramagnetic Curie temperature value characterizes the intensity of exchange interactions. The effective magnetic moments of the RNi compounds and hydrides practically do not change during hydrogenation and are very close to the magnetic moments values of free rare earth ions. We suppose that nickel atoms are non-magnetic in these compounds, and magnetic properties are caused by rare-earth metal atoms. Probably, the disappearance of the magnetic moment in transition metal sublattice is connected with the filling of a 3d-band of nickel atoms by electrons from the hydrogen atoms. The electron shell of nickel atoms ($3d^8$) is close to completed. The injection of hydrogen atoms' electrons in a 3d-band leads to its completion. As a result the 3d-subsystem magnetic moment becomes extremely small, exchange interaction strongly decreases. Therefore the magnetic properties depend on a subsystem of rare-earth metal atoms.

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