



# Influence of hydrogenation on magnetic interactions in intermetallic RNi (R = Gd, Tb, Dy) compounds

W. Iwasieczko<sup>a</sup>, H. Drulis<sup>a</sup>, Yu. L. Yaropolov<sup>b,\*</sup>, S.A. Nikitin<sup>b</sup>, V.N. Verbetsky<sup>b</sup>

<sup>a</sup> Trzebiatowski Institute of Low Temperature and Structure Research, Polish Academy of Sciences, 50-950 Wrocław, Poland

<sup>b</sup> Lomonosov Moscow State University, GSP-3, Leninskije Gory, Moscow, 119992, Russia

## ARTICLE INFO

### Article history:

Received 29 July 2010

Received in revised form 11 October 2010

Accepted 26 October 2010

Available online 2 November 2010

### Keywords:

Rare earth compounds

Metal hydrides

Magnetic measurements

## ABSTRACT

The influence of hydrogenation on the magnetic properties of intermetallic compound RNi is reported. GdNiH<sub>3.2</sub>, TbNiH<sub>3.4</sub>, DyNiH<sub>3.4</sub> hydrides have been synthesized and their magnetic properties were investigated in the temperature range 1.8–300 K. It was established that hydrogen absorption in these compounds makes the ferro- and antiferromagnetic interactions between magnetic moments much weaker. The reasons of this phenomenon are discussed. The hydrogen presence at interstitial positions also changes the symmetry of the crystal electric field at the rare earth ion sites making this symmetry higher than those in initial intermetallics.

© 2010 Elsevier B.V. All rights reserved.

## 1. Introduction

The magnetic transition temperatures of many rare earth intermetallic compounds and alloys are very sensitive on hydrogen presence in the crystal lattice. Hydrogenation can change the electronic structure of the compound as well. Good examples are the rare earth R<sub>2</sub>Fe<sub>17</sub>, RFe<sub>11</sub>Ti compounds – with high content of iron [1,2]. The apparent Curie transition temperature enhancement due to the large increase of unit cell volume after hydrogenation is observed. The enhancement of magnetic interaction can partly be caused by the changes of the 3d electronic density of state (DOS) at the Fermi level. In the hydrogen protonic (H<sup>+</sup>) model, the conduction band can be filled in by an additional number of the conduction electrons coming from hydrogen atoms or might be depopulated in an anionic (H<sup>−</sup>) hydrogen ion version.

Magnetic properties of the RNi compounds have already been studied relatively in detail [3–7]. RNi compounds with R = Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm are ferromagnets with transition temperatures  $T_C$  in the region of the liquid nitrogen temperature. On the other hand, the several compounds of series YNi, LaNi, CeNi, YbNi and LuNi are Pauli paramagnets. This indicates that the nickel atom is a nonmagnetic ion and that all magnetism is coming from the rare earth atoms when RE is the magnetic element. Some of the magnetically active compounds are believed to be important for the magnetocaloric cooling or heating effects – for instance, GdNi, DyNi, HoNi and ErNi which have shown a high magnetocaloric

effect at magnetic phase transition temperatures [6,7]. The field dependence of the magnetization of some RNi compounds shows an additional metamagnetic transition at temperatures lower than  $T_C$  [5–7]. The strong anisotropy of the magnetic properties is also observed in these compounds.

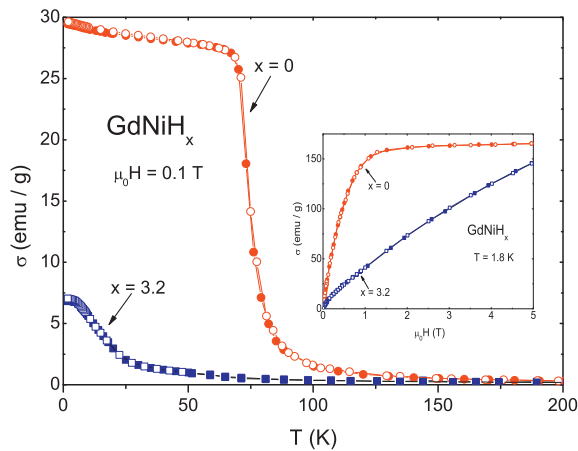
The magnetic moments of the rare earth elements (except Gd) are ordered non-collinearly, and apart from a ferromagnetic component, there is also an antiferromagnetic component which has a direction different to the ferromagnetic one [4,8,9]. This type of magnetic structure appears as a result of competition between exchange magnetic interactions and the magnetocrystalline anisotropy caused by the energy levels of the rare earth ions split due to the crystal electric field interaction. The presence of an antiferromagnetic component may cause the spin-reorientation transitions in the external magnetic field oriented along some chosen direction. This can be visible as characteristic steps on the magnetization curve versus the magnetic field.

The magnetic properties of the RNi (R = Gd, Tb and Dy) hydride phases have not been widely reported up to now. The preliminary magnetic measurements of the RNi (R = Gd, Tb and Dy) hydride phases have been reported in Ref. [10]. In [9] the temperature dependence of magnetization of the CeNi compound and its hydride phase were studied. The CeNiH<sub>2.9</sub>-hydride phase is a paramagnetic material with paramagnetic Curie temperature  $T = -19$  K. The magnetic moment calculated per Ce atom  $\mu_{\text{eff}} = 2.46\mu_B$  is very close to the magnetic moment of the free Ce<sup>3+</sup> ion equal of  $\mu_{\text{eff}} = 2.54\mu_B$ .

The aim of this report is to study the magnetic properties of the RNi (R = Gd, Tb and Dy) hydride phases in the temperature range 1.8–300 K much wider than it was done in [10].

\* Corresponding author. Tel.: +7 495 939 1413; fax: +7 495 932 8846.

E-mail address: [yaropolov@inbox.ru](mailto:yaropolov@inbox.ru) (Yu.L. Yaropolov).



**Fig. 1.** Temperature dependence of magnetization for GdNiH<sub>3.2</sub> hydride and GdNi compound for FC (open symbols) and ZFC (closed symbols) procedures. The inset shows the field dependence of magnetization at 1.8 K.

## 2. Experimental details

The rare earth nickel intermetallic compounds were prepared by arc-melting stoichiometric amounts of the constituent elements. Nickel (purity of 99.99%) and rare earth metals (99.9%) were used. For good homogeneity, the ingots were turned and re-melted several times. The hydrogenation of intermetallic samples was carried out using a Sieverts-type apparatus. The composition of the hydride samples were determined by a volumetric method based on the comparison of the gas pressure before and after hydrogen absorption. The hydrogen reacts with GdNi, TbNi, and DyNi compound relatively quickly. The GdNiH<sub>3.2</sub>, TbNiH<sub>3.4</sub>, DyNiH<sub>3.4</sub> hydrides have been obtained at room temperature under hydrogen pressure lower than 0.1 MPa. The crystal structure and phase purity of the sample were analyzed by the powder X-ray diffraction in [10]. This analysis showed that the GdNi crystallizes in the orthorhombic CrB-type structure (*Cmcm* space group), DyNi crystallizes in the orthorhombic FeB-structure (*Pnma* space group), whereas TbNi possess his own structure type (*P2<sub>1</sub>/m* space group). All the hydride samples crystallize in the CrB-type structure. An increase of the crystal unit-cell volume of about 24–25% on average was found for all hydrides under study.

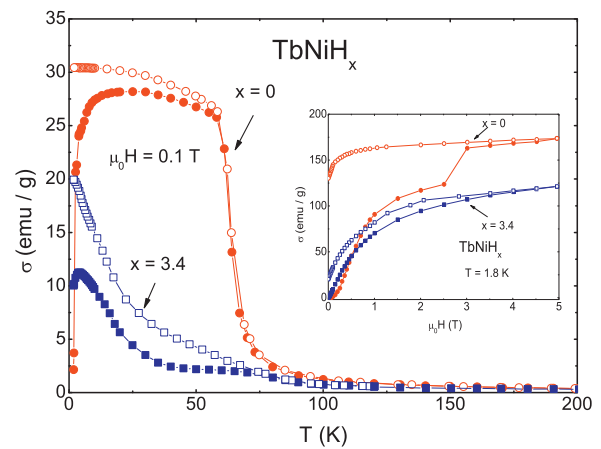
The magnetization measurements in the temperature range of 1.8–300 K were carried out in zero field (ZFC) and field cooling (FC) procedures in a field of  $\mu_0 H = 0.1$  Tesla (T) with the SQUID Quantum Design equipment. The magnetization isotherm measurements were performed in the field range 0–5 T at the lowest temperature  $T = 1.8$  K.

## 3. Results and discussion

The results of magnetization measurements as a function of temperature for GdNiH<sub>3.2</sub>, TbNiH<sub>3.4</sub>, DyNiH<sub>3.4</sub> hydrides, and their initial GdNi, TbNi and DyNi compounds for FC and ZFC procedures are presented in Figs. 1–3, respectively. In the insets, the respective magnetization measurements made at 1.8 K in the magnetic fields up to  $\mu_0 H = 5$  T are shown. The Curie temperatures of the ferromagnetic transition of parent RNi alloys and their hydride were estimated from the  $\sigma(T)$  curves taken for FC version of measurements. The spontaneous magnetic moments were estimated from magnetization  $\sigma(H)$  isotherms at 1.8 K. The results of the magnetic investigations are collected in Table 1. From this data,

**Table 1**  
Magnetic data for GdNiH<sub>3.2</sub>, TbNiH<sub>3.4</sub>, DyNiH<sub>3.4</sub> hydrides and they corresponding RNi compounds.

Compound	$T_C$ (K)	Spontaneous moment at 1.8 K
DyNi	59	4.40
DyNiH <sub>3.4</sub>	3.5	4.60
TbNi	62	6.32
TbNiH <sub>3.4</sub>	3.5	3.77
GdNi	75	6.20
GdNiH <sub>3.2</sub>	10	–

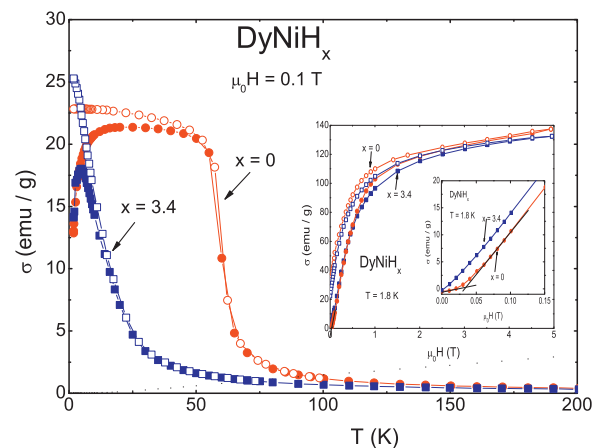


**Fig. 2.** Temperature dependence of magnetization for TbNiH<sub>3.4</sub> hydride and TbNi compound. In the inset the field dependence of magnetization at 1.8 K is shown. Symbol's description as in Fig. 1.

and as reported in [10] it appears that the nickel atoms have a non-magnetic configuration 3d<sup>10</sup> in both the hydride phase and in initial 1:1 compounds. The whole magnetism of the hydride and respective alloys is determined by the rare earth ion magnetic moments. However, it is interesting to point out that the ordering temperatures of the hydrides are lower than those in corresponding RNi compounds. These lower Curie temperature values reflect the weakening of the ferromagnetic R–R exchange interactions after RNi hydrogenation.

The temperature dependence of magnetization of GdNiH<sub>3.2</sub> hydrides shown in Fig. 1 indicates that it behaves like a ferromagnet similarly to its parent compound. However, the plots in the insets of Fig. 1 show that the magnetization of GdNiH<sub>3.2</sub> at 1.8 K does not approach the saturation state even at the highest field applied, whereas GdNi reaches the magnetic saturation already in the field  $\mu_0 H = 1.5$  T. It is worth to stress that there is no differences between the FC and ZFC magnetization in both gadolinium compounds.

The temperature dependence of magnetization for TbNiH<sub>3.2</sub> and TbNi alloy in Fig. 2 shows that there is an essential difference between ZFC and FC measurements below 60 K. This is likely connected with the presence of large magnetocrystalline anisotropy, particularly in the TbNi sample. The magnetization isotherm in TbNiH<sub>3.4</sub> hydrides in Fig. 2 approaches saturation at a field of 5 T, like its initial compound, but the magnetization value is of 50% less.



**Fig. 3.** Magnetization measurements as a function of temperature and magnetic field for DyNiH<sub>3.4</sub> hydride and DyNi alloy. In the inset the details of magnetization for the lowest magnetic fields are displayed. Symbols description as in Fig. 1.

It is important to note that there is no evidence for the metamagnetic or spin reorientation transitions in the TbNiH<sub>3.4</sub> hydride phase, which were observed in TbNi alloy at about 0.5 T and 2.5–3 T magnetic fields. It is obvious that the fields of  $\mu_0 H > 3.0$  T destroy the subtle magnetic structure of Tb moments in TbNi alloy. The antiferromagnetic component of this structure, which exists at zero field, disappears and a full collinear ferromagnetic ordering is established.

The temperature dependence of the magnetization for DyNi and DyNiH<sub>3.4</sub> hydrides in Fig. 3 are similar to the dependencies in the terbium compounds. However, from the dependence of magnetization on the magnetic field shown in the inset of Fig. 3 appears that metamagnetic or spin re-orientation transitions in DyNi alloy takes place at very low magnetic fields contrary to those observed in TbNi compound.

#### 4. Conclusions

From our investigations presented in this report, we have come to the following conclusions:

1. Introduction of hydrogen atoms to the RNi compounds increases the crystal unit cell volume and changes its structure type in the case of TbNi and DyNi. However, this fact does not induce the appearance of magnetic moment on the nickel ions in the hydride phase as one can expect.
2. The hydrogen atoms seems to be electron donors (the vice-versa situation should not be excluded). Nevertheless, the filling or depopulation of the conduction band of RNi with electrons diminishes the magnitude of electron density of state (DOS) at the Fermi energy level. In such a way, according to the RKKY coupling model, the exchange interaction between the rare earth 4f magnetic moments is reduced and the magnetic transition temperatures are dramatically lowered in the hydride phases.
3. The hydrogen presence at interstitial positions changes also the symmetry of crystal electric field at the rare earth ion sites making this symmetry higher. Unfortunately, hydrogen ions occupy interstitial sites rather statistically and the symmetry of electric field potentials is somehow distributed more than those in the initial compounds. In this case, the role of magnetocrystalline anisotropy in the magnetic ordering processes in TbNi and DyNi hydride samples is diminished or even canceled. This results in the lack of a tendency for the metamagnetic transitions in the hydride phases to take place.
4. Upon analyzing the different magnetization characteristics for GdNi in comparison to those in TbNi and DyNi, it is evidently seen that the non-collinear magnetic structure in the two latter compounds arise from a competition between the exchange interaction and the magnetocrystalline anisotropy. Gd<sup>3+</sup> ion has an angular orbital moment  $L=0$ , therefore there should not be any magnetocrystalline anisotropy and indeed GdNi appears as a pure ferromagnetic compound. On the other hand, the field dependence of magnetization for GdNiH<sub>3.2</sub> at 1.8 K in Fig. 1 suggests that the hydride behaves rather as a ferrimagnetic material.

#### References

- [1] S.A. Nikitin, I.S. Tereshina, V.N. Verbetsky, A.A. Salamova, J. Alloys Compd. 316 (1–2) (2001) 46–50.
- [2] I.S. Tereshina, S.A. Nikitin, V.N. Verbetsky, A.A. Salamova, J. Alloys Compd. 336 (2002) 36–40.
- [3] R.E. Walline, W.E. Wallace, J. Chem. Phys. 416 (1964) 1587–1591.
- [4] S.C. Abrahams, J.L. Bernstein, R.C. Sherwood, J.H. Wernick, H.J. Williams, J. Phys. Chem. Sol. 25 (10) (1964) 1069–1080.
- [5] S. Matas, M. Mihalik, M. Zentkova, Acta Phys. Pol., A 113 (1) (2008) 319–322.
- [6] S.K. Tripathy, K.G. Suresh, R. Nirmala, A.K. Nigam, S.K. Malik, Solid State Commun. 134 (5) (2005) 323–327.
- [7] P. Kumar, K.G. Suresh, A.K. Nigam, O. Gutfleisch, J. Phys. D: Appl. Phys. 41 (2008) 245006.
- [8] D. Gignoux, J. Phys. 35 (1974) 455.
- [9] J.-L. Bobet, E. Grigorova, B. Chevalier, M. Khrussanova, P. Peshev, Intermetallics 14 (2) (2006) 208–212.
- [10] Yu.L. Yaropolov, V.N. Verbetsky, A.S. Andreenko, K.O. Berdyshev, S.A. Nikitin, Inorg. Mater. 46 (2010) 364–371.