DEVELOPMENT OF MAGNETISM UNDER HYDROGENATION IN *RE*NiAl–H SYSTEMS

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The paper is devoted to the study of effect of hydrogenation (deuteration) on magnetic properties of *RE*NiAl compounds (*RE* = rare–earth atom). It was found that incorporation of hydrogen into the crystal lattice drastically reduces magnetic ordering temperatures in these materials due to modification of the density of electronic states at the Fermi level. Hydrogen differential thermal analysis (HDTA) studies show that hydrogen occupies 2 or 3 different crystallographic positions in the unit cell, which is in agreement with the results of neutron diffraction. Removal of hydrogen from the lattice leads to a non–contionuous recovery of the original magnetic and crystal properties of *RE*NiAl.

Key words: rare earth metals, magnetism, hydrides, deuterides, decomposition.

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I. INTRODUCTION

Hydrogen was found to be a unique tool strongly affecting both crystal lattice and the density of electronic states (DOS) in *RE*NiAl (*RE* = rare–earth atom) compounds [1]. This variation leads to a weakening of RKKY exchange interaction, which defines magnetic properties of rare–earth intermetallic compounds with highly localised 4*f*–states. The weakening of the exchange interactions induces either a decrease of ordering temperatures (*e.g.* T_C = 59 K in GdNiAl decreases down to 20 K in $GdNiAlH_{1.35}$), or a decrease of temperature independent magnetic susceptibility in Pauli paramagnets YNiAl and LuNiAl by approximately two orders of magnitude [2]. It is worth mentioning that these changes were observed in hydrides obtained already at relatively low hydrogen pressure of 1 bar and at room temperature.

As a continuation of the systematic studies of the *RE*NiAl–based hydrides, in this paper we present crystal structure data and magnetic properties of the saturated hydrides of Sm– and Tm–containing compounds, $SmNiAlH_{1.2}$ and $TmNiAlH_{1.4}$. We will also focus on the results of crystallographic and magnetic studies of TbNiAl–H, YNiAl–H, ErNiAl–H and GdNiAl–H systems showing how the hydrogen content affects their properties. The observed changes in magnetic properties will be analysed as related to the modification of the original crystal structure and the reconstruction of DOS due to H–bonding.

II. EXPERIMENTAL DETAILS

The preparation of hydrides and their X–ray characterisation is described elsewhere [1]. Synthesis was performed at room temperature and 1 bar H_2 loading pressure using a volumetric method.

Hydrogen Differential Thermal Analysis equipment (see [3] for the details) at a heating rate of 5 K/min was used in studies of the thermal stability of hydrides. In order to define the peak positions in $SmNiAlH_{1.2}$ we have used the curve fitting routine assuming the Gaussian shape of peaks.

Faraday balance and SQUID magnetometer have been used for magnetic studies. The Oxford Instrument Faraday balance gives the possibility to reach temperatures within the range of 1.8–300 K and fields up to 7 T. Quantum Design SQUID magnetometer provides temperatures down to 5 K and magnetic fields up to 5 T. In all cases the magnetic measurements were performed on randomly oriented powders fixed by glue in a quartz crucible.

III. RESULTS AND DISCUSSION

Similarly to other *RE*NiAl hydrides [2], the crystal lattice of $SmNiAlH_{1.2}$ and $TmNiAlH_{1.4}$ (see Table 1) is expanded in the basal plane and contracted along the *c*–axis. No orthorhombic distortion, which is characteristic for a number of *RE*NiAl–based saturated (1 bar H_2) hydrides [2], was observed for *RE* = Sm, Tm. Hydrogenation results in the increase of the unit cell volume by 4.7 % in $TmNiAlH_{1.4}$ and 8.7 % in $SmNiAlH_{1.2}$, the last value being the highest one for the $RENiAlH_X$.

For $SmNiAlH_{1.2}$, $TmNiAlH_{1.4}$, $TbNiAlH_{1.4}$ [2] we have studied hydrogen desorption in order to specify their stability as well as to obtain materials with lower hydrogen content. For this purpose we have used the HDTA technique. The HDTA spectrum of *RE*$NiAlH_X$ typically exhibits two or more peaks (see Fig. 1 as an example). According to [4], the presence of multiple peaks on HDTA curve can be interpreted as the consequence of several phenomena, including 1) desorption of hydrogen from nonequivalent crystallographic positions with different bonding energies or 2) dependence of the metal–H bonding energy on hydrogen content.

Hydride	a, Å	b, Å	c, Å	$\Delta V/V$,%	$\Delta a/a$,%	$\Delta c/c$,%
YNiAl	7.036(1)	—	3.839(1)	—	—	—
$YNiAlH_{0.14}$	7.055(3)	—	3.876(4)	1.5	0.3	1.0
$YNiAlH_{0.9}$	7.1005(6)	—	3.890(2)	3.2	0.9	1.4
SmNiAl	6.979(3)	—	4.0247(8)	—	—	—
$SmNiAlH_{1.2}$	7.50(1)	—	3.776(3)	8.7	7.4	-5.8
GdNiAl	7.0125(8)	—	3.9140(9)	—	—	—
$GdNiAlH_{0.14}$	7.097(5)	—	3.930(10)	2.8	1.2	0.4
$GdNiAlH_{0.6}$	7.125(5)	—	3.903(7)	2.9	1.6	-0.3
$GdNiAlH_{1.35}$*	7.636(4)	12.378(1)	3.736(2)	5.9	8.9	-4.5
ErNiAl	6.970(2)	—	3.8003(6)	—	—	—
$ErNiAlH_{0.5}$	6.973	—	3.840	1.1	0.04	1.0
$ErNiAlH_{0.8}$	7.0322	—	3.831	2.6	0.9	0.8
TmNiAl	—	6.964(2)	3.789(1)	—	—	—
$TmNiAlH_{1.4}$	7.210(1)	—	3.700(2)	4.7	3.5	-2.3

Table 1. Crystallographic characteristics of the *RE*$NiAlH_X$ hydrides. Crystallographic characteristics of the *RE*$NiAlH_X$ hydrides. *All *RE*NiAl and *RE*$NiAlH_x$ compounds crystallise in hexagonal ZnNiAl–type structure (space group $P\overline{6}2m$) except for $GdNiAlH_{1.35}$, which has orthorhombically distorted parent structure (space group Amm2).

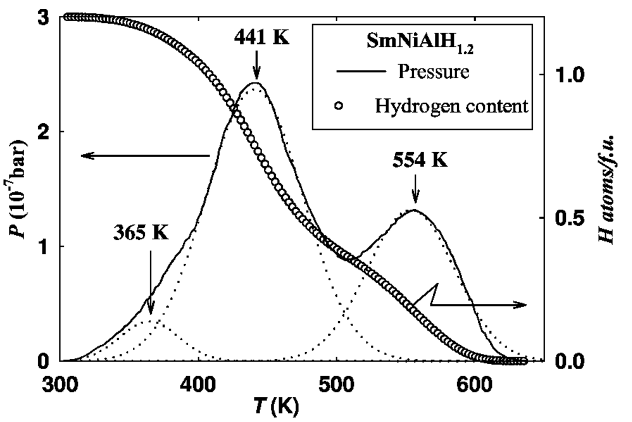

Fig. 1. HDTA traces of hydrogen desorption from $SmNiAlH_{1.2}$. Note two vertical axes. The dotted lines show the peaks obtained by curve fitting.

In all cases these peaks are located between the room temperature and approximately 750 K. By that temperature decomposition is completed. This was confirmed by the X–ray diffraction data, showing good agreement between the cell parameters of the materials after H–desorption and those of the corresponding parent RE-NiAl compound.

The HDTA spectrum of $SmNiAlH_{1.2}$ has three peaks at 365 K, 441 K and 554 K (Fig. 1). The first peak at 365 K is masked by hydrogen desorption event from the site with the highest hydrogen occupancy (at 441 K). The HDTA spectrum of $TmNiAlH_{1.4}$ has only two peaks at 403 K and 643 K (Fig. 2), that correspond to hydrogen removal from two different crystallographic sites with almost equal hydrogen occupancy.

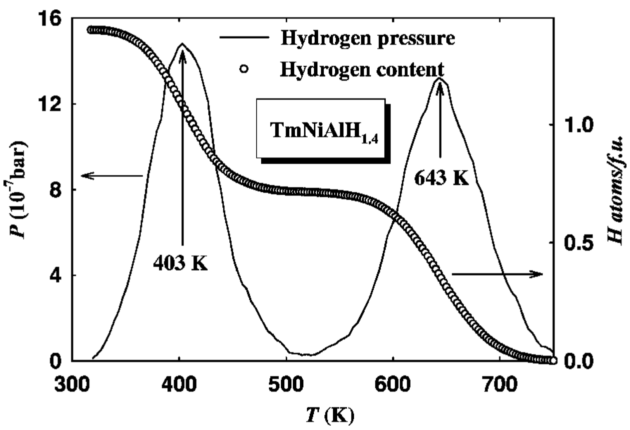

Fig. 2. HDTA traces of hydrogen desorption from $TmNiAlH_{1.4}$. Note two vertical axes.

For explanation of the phenomena that are taking place in *RE*$NiAlH_X$, the neutron diffraction studies of *RE*NiAl–based deuterides are very useful. Results of the neutron studies of the TbNiAl–based deuterides were published recently for $TbNiAlD_{1.28}$ [5], $TbNiAlD_{1.1}$ [6],

$TbNiAlD_{1.04}$ [7], $TbNiAlH_{0.8}$ [5] and $TbNiAlD_{0.3}$ [7]. It was found that a number of crystallographically different hydrides is formed in a narrow range of D/TbNiAl contents limited by a rather small D concentration in the saturated deuteride $TbNiAlD_{1.4}$. Three types of interstitial positions are filled in $TbNiAlD_{1.1}$ [6] and $TbNiAlD_{1.04}$ [7], including Tb_3Ni_2 trigonal bipyramid and two kinds of Tb_2NiAl tetrahedra, one of which is the same and the other one is different for these two deuterides. Two positions with the highest occupation numbers ($TbNiAlD_{1.1}$ [6] and $TbNiAlD_{1.04}$ [7]) were found to be filled in the $TbNiAlD_{1.28}$ [5]. Such experimental observations indicate a significant flexibility of the D–sublattice and are presumably caused by a weak bonding of D atoms in the Tb_2NiAl positions [7]. At the smallest D contents studied deuterium is completely removed from the Tb_2NiAl sites and the hexagonal superstructure $TbNiAlD_{0.3}$ is formed by an ordered occupation of one half of the available Tb_3Ni_2 bipyramids [7].

Studies of the crystal structure [2, 5–7] have also shown that decrease of the hydrogen (deuterium) content is accompanied by decrease of the orthorhombic distortion. For $TbNiAlH_{1.4}$ the relation between the unit cell parameters is $b/a = 0.934\sqrt{3} = 1.618$, for $TbNiAlD_{1.28}$ $b/a = 0.936\sqrt{3} = 1.621$ [5], while in $TbNiAlH_{1.04}$ b/a decreases to $0.986\sqrt{3} = 1.708$ [7] and for the deuteride with the lowest D contents, $TbNiAlD_{0.3}$, the hexagonal symmetry is restored [7].

The SmNiAl has two magnetic phase transitions at $T = 20$ K and 16 K [8], but after the uptake of 1.2 H atoms/f.u. only one transition can be observed at $T = 5$ K (see Fig. 3). High–temperature part of the magnetic susceptibility does not follow the Curie–Weiss law.

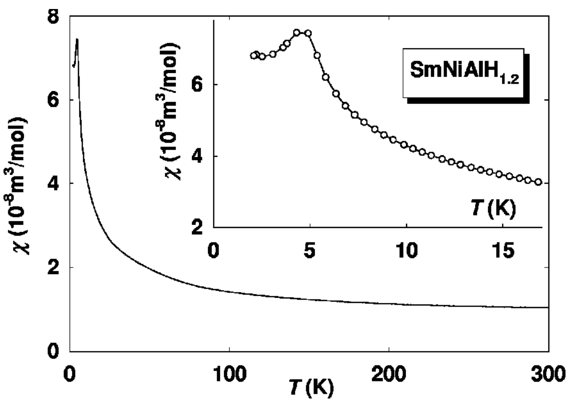

Fig. 3. Temperature dependence of magnetic susceptibility $\chi(T)$ measured on $SmNiAlH_{1.2}$ in the field of 1 T.

Hydrogenation has similar effect on the magnetic properties of TmNiAl (Fig. 4): its hydride does not show any magnetic order down to 5 K. Curie–Weiss law describes the magnetic susceptibility $\chi(T)$ down to 20 K. Below this temperature $\chi(T)$ becomes weakly field dependent. The value of the paramagnetic Curie temperature Θ_P obtained from the fit in the high–T region is 3 K both for TmNiAl and $TmNiAlH_{1.4}$. The effective moments μ_{eff} are somewhat different: 7.7 μ_B/f.u. and 7.0 μ_B/f.u. before and after the hydrogenation, respectively.

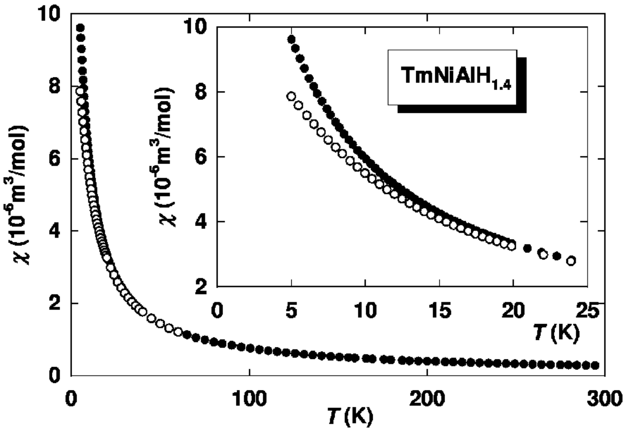

Fig. 4. Magnetic susceptibility χ vs. temperature for $TmNiAlH_{1.4}$. The insert shows the low temperature data in the fields of 1 T (filled circles) and 2 T (empty circles).

The changes of magnetic properties in SmNiAl and TmNiAl under hydrogenation strongly resemble the tendency observed in the rest of the *RE*NiAl series, indicating the weakening of the exchange interaction. For instance, the temperature dependence of magnetic susceptibility of the saturated hydride $TbNiAlH_{1.4}$ shows only one phase transition at 14.5 K [2]. On the other hand, "lower" hydride $TbNiAlH_{0.7}$ has two phase transitions at the temperatures close to those of TbNiAl, *i.e.* 45 K and 24 K (48 K and 24 K in TbNiAl).

In the YNiAl–H system we obtained two lower hydrides with 0.95 and 0.21 H atoms/f.u. Both of them have hexagonal unit cells, so that in this system the orthorhombic distortion disappears already after the release of 20 % of hydrogen from the saturated hydride. This is much less than the values for TbNiAl–D system, where even after the desorption of 50 % of hydrogen the unit cell is still orthorhombically distorted. It is also notable that even for $YNiAlH_{0.21}$ the unit cell volume is bigger by 1.5 %, compared to the parent compound, assuming that charge redistribution is an important mechanism of the unit cell distortion upon hydrogenation.

Two lower hydrides from the ErNiAl–H system with 0.81 and 0.44 H atoms/f.u. have hexagonal unit cells. For these compounds $\Delta V/V$ values are 2.6 % and 1.1 %, respectively (Table 1).

In the GdNiAl–H system hexagonal symmetry is restored after the release of approximately 20 % of hydrogen from the saturated $GdNiAlH_{1.35}$, so both $GdNiAlH_{1.06}$ and $GdNiAlH_{0.14}$ have hexagonal structures. The highest ordering temperatures of GdNiAl in the whole *RE*NiAl series allow more detailed investigation of the effect of hydrogen on magnetism. It is noteworthy that in spite of the different symmetries of the unit cell, $GdNiAlH_{1.35}$ and $GdNiAlH_{1.06}$ have the same ordering temperature T = 20 K (Fig. 5) . The difference is that $GdNiAlH_{1.06}$ has higher absolute values of magnetic susceptibility and does not show a maximum of $\chi(T)$ at 11 K.

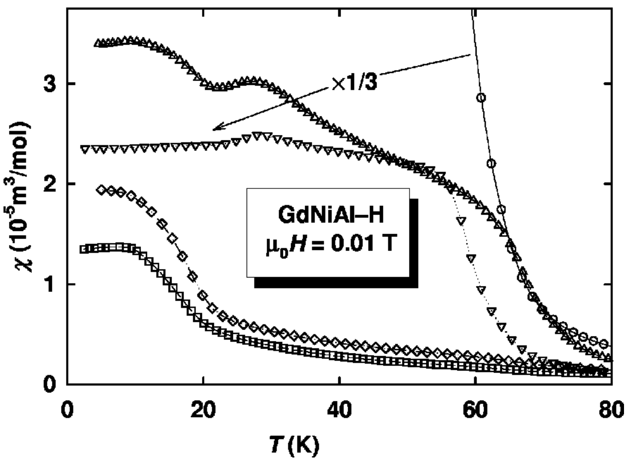

Fig. 5. Temperature dependencies of magnetic susceptibility χ for GdNiAl–H system in the field of 0.1 T. The data for GdNiAl (**O**), saturated hydride $GdNiAlH_{1.35}$ (◯) and two intermediate hydrides with 0.6 (◇) and 0.14 (△) H atoms/f.u. are shown on the plot. The data for GdNiAl had to be divided by 3 to fit within the same scale (▽). The lines are eye–guides.

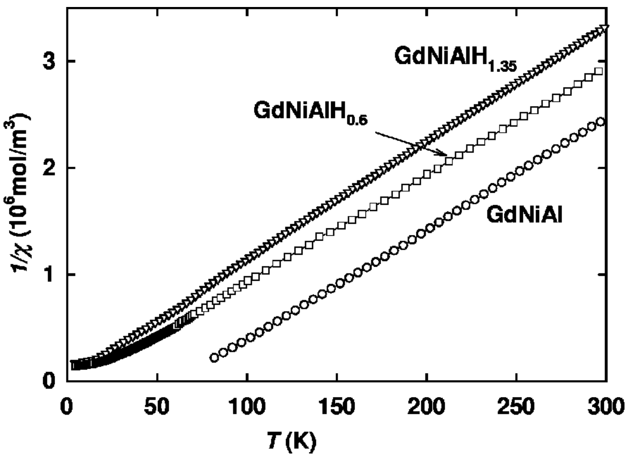

Fig. 6. Inverse susceptibility vs. temperature for GdNiAl–H system in the field of 1 T. The data for $GdNiAlH_{1.35}$ is shown by empty triangles, for $GdNiAlH_{0.6}$ — by empty squares and for GdNiAl — by empty circles. The lines are eye–guides.

The comparison of the $1/\chi$ temperature dependencies of GdNiAl, its saturated hydride $GdNiAlH_{1.35}$ and lower hydride $GdNiAlH_{1.06}$ (Fig. 6) shows that the features observed for the last compound are intrinsic, but not a linear combination of $1/\chi(T)$ of parent intermetallic and saturated hydride. If the latter was the case, temperature dependence of inverse susceptibility for $GdNiAlH_{1.06}$ would show anomaly around 60 K since Θ_P = 62 K for GdNiAl. The curve fitting of temperature dependence of magnetic susceptibility to Curie–Weiss law yields similar values of paramagnetic Curie temperature and effective moment for saturated hydride and partially decomposed hydride: Θ_P = -1.5 K and 8 K and μ_{eff} = 7.6 μ_B/f.u. and 7.9 μ_{eff} = 7.6 μ_B/f.u., respectively. Further hydrogen desorption up to 563 K leads to formation of $GdNiAlH_{0.14}$, which strongly resembles GdNiAl: it has three magnetic phase transitions at 66 K, 27 K and 21 K (compared with 59 K, 28 K and 22 K for GdNiAl). The absolute values of $\chi(T)$ are almost 3 times lower for $GdNiAlH_{0.14}$ than for the parent intermetallic.

IV. CONCLUSIONS

Hydrogen desorption and neutron diffraction studies indicate that in *RE*$NiAlH_X$ compounds hydrogen occupies several crystallographic positions with different bonding energies. It is possible to remove hydrogen atoms from the crystal lattice in a step–wise manner and to obtain intermediate hydrides with preferential occupation of certain crystallographic sites by H atoms. The orthorhombic distortion vanishes when the H content reaches some critical value, but the unit cell expansion persists even in the hydrides with the lowest hydrogen concentration.

The decrease of magnetic ordering temperatures in the *RE*NiAl–H series upon hydrogenation reflects the weakening of the exchange interaction. The absolute values of paramagnetic Curie temperature, which is proportional to the strength of the exchange, are also lower for hydrides than for parent *RE*NiAl compounds. Hydrogen desorption leads to a step–wise recovery of the original magnetic properties. What is notable is that magnetic behaviour, *i.e.* ordering temperatures, of the hydrides with low hydrogen content are similar to that of parent compounds, despite the crystal lattice is already expanded (the case of $GdNiAlH_{0.14}$). But unit cell deformation and symmetry changes due to hydrogenation have only minor effect on magnetic properties: for instance the behaviour of $GdNiAlH_{1.35}$ and $GdNiAlH_{1.06}$ is very much alike, though they have unit cells of different symmetry. Based on this we assume that the modification of the density of electronic states under hydrogenation has the strongest effect on the magnetic properties of *RE*NiAl. Magnetic exchange in these compounds with highly localised $4f$ states is described by RKKY model, in which the exchange strength depends, alongside with other factors, on the concentration of the conduction electrons and the value of local magnetic moments. Since the values of μ_{eff} are very close for the parent intermetallics and for the hydrides, that should be the decrease of the concentration of conduction electrons that affects the magnetic exchange. Hence, the hydrogenation should reduce $N(E_F)$ value. This is confirmed by the decrease of the absolute values of magnetic susceptibility in Pauli paramagnets YNiAl and LuNiAl under hydrogenation.

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[1] A. V. Kolomiets, L. Havela, V. A. Yartys, A. V. Andreev, J. Alloys Comp. **253–254**, 343 (1997).

[2] A. V. Kolomiets, L. Havela, V. A. Yartys, A. V. Andreev, J. Phys. Stud. **3**, 55 (1999).

[3] D. Book, I. R. Harris, J. Alloys Comp. **221**, 187 (1995).

[4] M. H. Mintz, I. Jacob, D. Shaltiel, in: *Topics in Applied Physics, vol. 67*, edited by L. Schlapbach (Springer Verlag, 1992), p. 304.

[5] H. N. Bordallo, H. Nakotte, J. Eckert, A. V. Kolomiets, L. Havela, H. Drulis, W. Iwasieczko, J. Appl. Phys. **83**, 6986 (1998).

[6] V. A. Yartys, F. Gingl, K. Yvon, L. G. Akselrud, A. V. Kolomietz, L. Havela, T. Vogt, I. R. Harris, B. C. Hauback, J. Alloys Comp. **279**, L4 (1998).

[7] B. C. Hauback, L. Pålhaugen, V. A. Yartys, H. Fjellvåg, K. Yvon, in: *International Symp. on Metal Hydrogen Systems. Fundamentals and Applications, Abstract Booklet. Hangzhou, China, October 4–9, 1998, F2:14P*, accepted for publication in J. Alloys Comp.

[8] N. C. Tuan, V. Sechovský, M. Diviš, P. Svoboda, H. Nakotte, F. R. de Boer, N. H. Kim–Ngan, J. Appl. Phys. **73**, 5677 (1993); Tuan, *PhD Theses* (Prague, Charles University 1992).

РОЗВИТОК МАГНЕТИЗМУ ПРИ НАВОДНЕННІ У *RE*NiAl–H СИСТЕМАХ

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Вивчено вплив наводнення (дейтерування) на магнетні властивості сполук типу *RE*NiAl (*RE* відповідає атомові рідкісноземельного металу). Виявлено, що втілення водню у кристалічну ґратку приводить до значного пониження температури магнетного впорядкування внаслідок зміни густини електронних станів на рівні Фермі. Дослідження методом водневого диференціяльного теплового аналізу свідчать, що водень займає 2 або 3 нееквівалентні кристалографічні позиції в елементарній комірці. Цей висновок підтверджується результатами нейтронної дифракції. Відновлення магнетних властивостей та кристалічної будови *RE*NiAl при видаленні водню із ґратки відбувається східчасто.