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*R*NiAl hydrides and their magnetic properties

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Abstract

*R*NiAl compounds absorb hydrogen at normal pressure typical to a stoichiometry of $R\text{NiAlH}_{\approx 1.4}$. Thermal desorption studies showed that, besides such hydrides, several partly decomposed hydrides with lower H concentrations are also stable. The X-ray analysis shows that, in most cases, hydrogenation leads to an orthorhombic distortion of the original hexagonal structure of the ZrNiAl type. The hydrogenation severely affects magnetic properties depressing ordering temperatures and changing all the magnetic phase diagrams. © 1997 Elsevier Science S.A.

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1. Introduction

Hydrogen has been found to be an interesting probe into the behaviour of *R*NiAl compounds (*R* = rare earth metal) crystallising in the hexagonal ZrNiAl-type of structure. Recently we have shown [1] that for some of these intermetallics, hydrogenation dramatically modifies crystal structures and magnetic behaviour. Unit cells of crystal structures of most saturated (1 bar H_2 pressure) $R\text{NiAlH}_{1.2-1.4}$ hydrides have been found to be orthorhombically distorted. Changes of interatomic distances in the hydrogenated compounds accompanied by modifications of electronic structures provide a weakening of exchange interactions. For example, the highest magnetic ordering temperature found for GdNiAl (59 K) is reduced in the corresponding $\text{GdNiAlH}_{1.35}$ hydride to 20 K. Another evidence of H-induced changes to magnetism are paramagnetic YNiAl and LuNiAl intermetallics where the Pauli susceptibility is reduced in both cases by two orders of magnitude, i.e. down to $\chi_0 \approx 10^{-11}\ \text{m}^3\ \text{mol}^{-1}$ and $\chi_0 \approx 10^{-13}\ \text{m}^3\ \text{mol}^{-1}$, respectively, upon hydrogen absorption.

In this work we present results of magnetic susceptibility studies obtained for two of the remaining *RE*NiAl compounds, i.e. SmNiAl and TmNiAl. Furthermore, as the decomposition studies point to the existence of several intermediate hydrides, we were able to follow the variations of magnetism with the H concentration decreasing below that of the saturated hydride. The development of magnetic properties of the GdNiAl-H system with varying H content is described.

2. Experimental details

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

Hydrogen Differential Thermal Analysis (HDTA)

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equipment (see [2] for the details) with a heating rate of 5°C min^{-1} was used in studies of the thermal stability of hydrides.

A Faraday balance and SQUID magnetometer were used for magnetic studies in field up to 6 T and in the temperature range 1.8–300 K. In all cases the magnetic measurements were performed on randomly oriented powders fixed by a glue in a quartz crucible.

3. Results and discussion

The original hexagonal symmetry is not changed upon the formation of $SmNiAlH_{1.20}$ and $TmNiAlH_{1.40}$. The unit cells are expanded in the basal plane with simultaneous contraction in the [001] direction. In the case of Sm-containing hydride a pronounced expansion of the cell in the [100] direction results in the highest value of the volume increase (8.7%) reached for all the series $RNiAlH_x$.

Crystallographic characteristics for all the hydrides studied are presented in Table 1.

For $SmNiAlH_{1.20}$ the antiferromagnetic transition could be observed at $T_N = 5$ K, see Fig. 1, while the parent intermetallic has two magnetic phase transitions at 20 K and 16 K [3]. Magnetic susceptibility of both SmNiAl and of its hydride decreases with increasing temperature but does not follow the Curie–Weiss law:

$$\chi = C/(T - \Theta_p),$$

where $C = N\mu_0\mu_B^2\mu_{eff}^2/3k_B$, N is the number of magnetic moments in 1 mol of material, $k_B =$ Boltzmann constant, $\mu_B =$ Bohr magneton, $\mu_{eff} =$ effective moment, $T =$ temperature, and $\Theta_p =$ paramagnetic Curie temperature.

After the hydrogenation, no magnetic ordering was observed for $TmNiAlH_{1.40}$ down to 5 K (Fig. 2). The susceptibility curve obeys the Curie–Weiss law down to 20 K. Below that temperature it becomes weakly field dependent. The fitting procedure gives the same Θ_p value as for TmNiAl, i.e. 3 K, while effective magnetic moments are somewhat different for the hydride (7.0 μ_B f.u.^{-1}) and parent intermetallic compound (7.7 μ_B f.u.^{-1}).

This effect of hydrogenation on magnetism in *R*NiAl with Tm and Sm resembles the development observed for other *RE*NiAl intermetallics studied before [1], which can be characterised by a weakening of magnetic interactions.

In order to specify the stability of hydrides, hydrogen vacuum desorption from the $TbNiAlH_{1.4}$, $GdNiAlH_{1.35}$, $YNiAlH_{1.2}$, and $ErNiAlH_{1.4}$ was studied.

Three or 4 peaks are indicated on the H-pressure curves in the HDTA spectra for the $RENiAlH_x$ hydrides under investigation (see example of GdNiAl-H in Fig. 3). In all cases, decomposition of hydrides is complete near 500°C. Total hydrogen removal from the metal lattice and a recovery of the hexagonal unit cells of the initial *R*NiAl intermetallics was proved by X-ray diffraction.

In accordance with thermal desorption spectroscopy approach, the presence of several distinct H-evolution events with different intensities can be interpreted in terms of (a) occupation of interstices with different metal surrounding and different radii and (b) changes in energy of metal-H bonds in a certain type of filled interstices depending on the hydrogen contents in the occupied position. Neutron diffraction studies are needed to clarify the distribution of hydrogen atoms in the crystal lattice of $RNiAlH_x$ hydrides as determined by hydrogen contents.

Table 1
Crystallographic characteristics of $RNiAlH_x$ hydrides

Hydride	*a* (Å)	*b* (Å)	*c* (Å)	Δv/v (%)	Δ*a*/*a* (%)	Δ*c*/*c* (%)
$YNiAlH_{1.2}$	7.602 (4)	12.353 (7)	3.713 (4)	5.9	8.0	−3.3
$YNiAlH_{0.95}$	7.1005 (6)	—	3.890 (2)	3.2	0.9	1.4
$YNiAlH_{0.21}$	7.055 (3)	—	3.876 (4)	1.5	0.3	1.0
$SmNiAlH_{1.20}$	7.50 (1)	—	3.776 (3)	8.7	7.4	−5.8
$GdNiAlH_{1.35}$	7.636 (4)	12.378 (1)	3.736 (2)	5.9	8.9	−4.5
$GdNiAlH_{1.06}$	7.125 (5)	—	3.903 (7)	2.9	1.6	−0.3
$GdNiAlH_{0.35}$	7.097 (5)	—	3.930 (10)	2.8	1.2	0.4
$ErNiAlH_{1.4}$	7.4804 (3)	12.3298 (5)	3.6888 (5)	6.4	7.3	−2.9
$ErNiAlH_{0.81}$	7.0322 (9)	—	3.831 (1)	2.6	0.9	0.8
$ErNiAlH_{0.44}$	6.973 (6)	—	3.840 (8)	1.1	0.04	1.0
$TmNiAlH_{1.40}$	7.210 (1)	—	3.700 (2)	4.7	3.5	−2.3
$TbNiAlH_{1.4}$	7.636 (1)	12.353 (2)	3.7209 (7)	6.6	9.1	−4.1
$TbNiAlH_{0.4}$	7.034 (1)		3.897 (1)	1.5	0.5	0.5
$TbNiAlD_{0.7}$	14.5195 (5)	12.4480 (3)	3.8022 (3)	4.4	3.7	−2.0

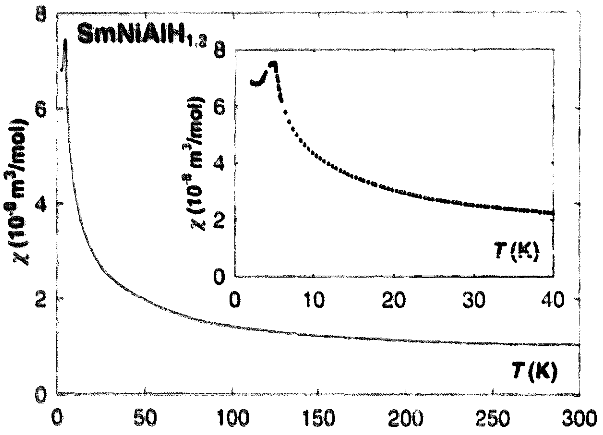

Fig. 1. Temperature dependence of magnetic susceptibility $\chi(T)$ measured on $SmNiAlH_{1.2}$ in the field of 1 T.

The lower hydrides in comparison with the saturated one were obtained during the HDTA experiments by interrupting the desorption of hydrogen after the pressure curve passed through a peak value and reached its local minimum.

Studies of the crystal structure and magnetic properties of $TbNiAlH_{0.7}$ and $TbNiAlD_{0.7}$ [1] showed that partial removal of hydrogen from saturated hydride significantly reduces a degree of orthorhombic distortion of the unit cell from $b/a = 1.618$ for $TbNiAlH_{1.4}$ to 1.715 for the $TbNiAlD_{0.7}$ which is very near to such a sequence in the hexagonal unit cell ($b_{orth}/a_{orth} = 1.732$). On further hydrogen removal, in $TbNiAlH_{0.4}$ the diffraction patterns are indexed in the hexagonal unit cell and the actual symmetry of the unit cell can be clarified only with use of neutron diffraction. An expected decrease of the volume expansion accompanies the transitions from higher to lower hydrides.

Magnetic properties are affected by changes of hydrogen contents as well: the temperature dependence of magnetic susceptibility of $TbNiAlH_{0.7}$ has already two magnetic phase transitions at temperatures very close to that of TbNiAl in contrast with the saturated $TbNiAlH_{1.4}$, which has only one phase transition shifted to lower temperatures.

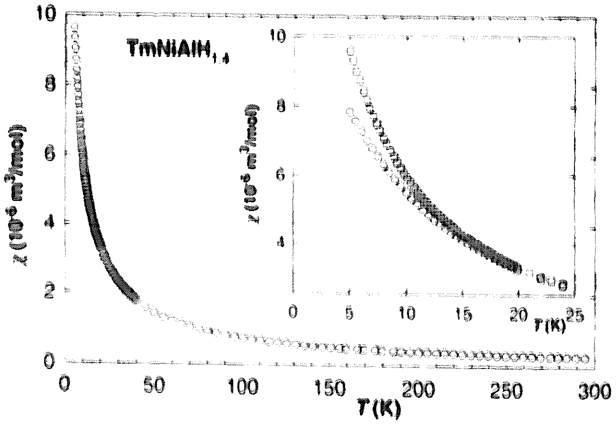

Fig. 2. Magnetic susceptibility χ vs. temperature for $TmNiAlH_{1.40}$. The inset shows the low temperature data in the fields of 1 T (empty squares) and 2 T (empty circles).

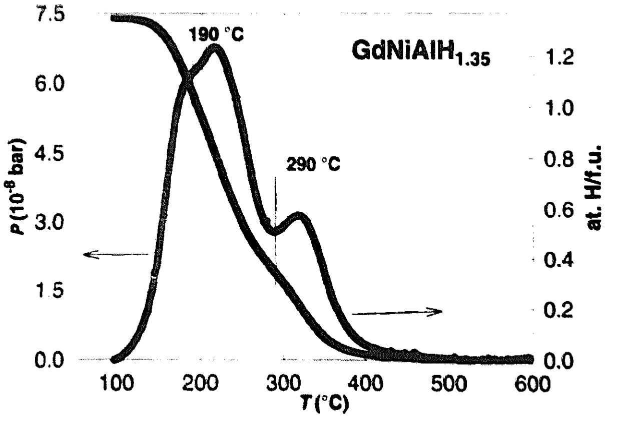

Fig. 3. HDTA traces of hydrogen desorption from $GdNiAlH_{1.35}$. The hydrogen pressure vs. temperature dependence obtained in the HDTA experiment with $GdNiAlH_{1.35}$ (left scale). The curve is corrected for the instrumental sloping background. Calculated corresponding amount of hydrogen in the unit cell relates to the right scale. Lines mark the two temperatures at which the intermediate hydrides mentioned in the text have been obtained.

For the YNiAl-H system, two intermediate hydrides were obtained with 0.95 and 0.21 H atoms per formula unit. Both of them have hexagonal unit cells and here the orthorhombic distortion is suppressed at higher H-concentrations compared to those in the Tb-containing hydrides. It is worth mentioning that even for the lowest YNiAl hydride with a relatively small concentration of hydrogen the unit cell is expanded by 1.5%. This fact can be interpreted as a result of charge redistribution caused by interstitial hydrogen which provides a modification of interatomic bonding.

The intermediate $ErNiAlH_{0.81}$ and $ErNiAlH_{0.44}$ hydrides have also been found to be hexagonal. The volumes of their unit cells are larger by 2.6% and 1.1%, respectively, than that of ErNiAl (see Table 1).

Similar trends were observed in the GdNiAl-H system, in which the saturated $GdNiAlH_{1.35}$ has an orthorhombic structure and after desorption of about 30% of hydrogen this distortion is suppressed, so that both $GdNiAlH_{1.06}$ and $GdNiAlH_{0.35}$ crystallise in hexagonal structures. Due to the higher ordering temperature of the Gd-containing compounds, a detailed investigation of magnetic properties was undertaken for this system. It was found that the magnetic susceptibilities of $GdNiAlH_{1.35}$ and $GdNiAlH_{1.06}$ (Fig. 4) have very similar shapes and show the magnetic transition at the same temperature $T = 20$ K. The difference is that $\chi(T)$ for $GdNiAlH_{1.06}$ reaches higher absolute values and no low-temperature maximum at $T = 11$ K is observed. Temperature dependence of the

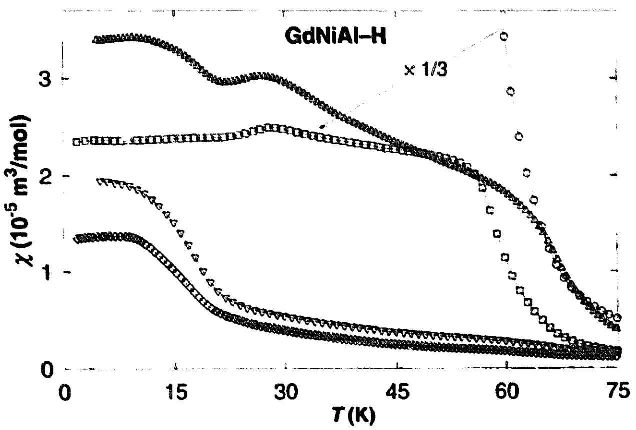

Fig. 4. Temperature dependencies of magnetic susceptibility χ for the GdNiAl-H system in the field of 0.1 T. The data for GdNiAl (○), saturated hydride $GdNiAlH_{1.35}$ (◇) and two intermediate hydrides with 1.06 (▽) and 0.35 H (△) atoms are shown on the plot. The data for GdNiAl had to be divided by 3 to fit within the same scale (□).

inverse magnetic susceptibility (Fig. 5) shows that $1/\chi$ of $GdNiAlH_{1.06}$ cannot be presented as a linear combination of inverse susceptibilities of saturated hydride and parent intermetallic, but is intrinsic to the partially decomposed hydride. The values of the paramagnetic Curie temperature and effective magnetic moment, obtained from fitting the magnetic susceptibility curve to the Curie–Weiss law, are quite similar: $\Theta_p = 8$ K (-1.5 K) and $\mu_{eff} = 7.9\ \mu_B$ f.u.$^{-1}$ (7.6 μ_B f.u.$^{-1}$) for the intermediate (saturated) hydride. On the other hand, the lowest intermediate hydride with 0.35 H atoms f.u.$^{-1}$ behaves very similarly to its parent intermetallic: it has three magnetic transitions at 66 K, 27 K, and 21 K (compare with 59 K, 28 K, and 22 K for GdNiAl), although the magnetic susceptibility in the ordered state has much lower absolute values, which suggests that the respective magnetic structures are different for GdNiAl and $GdNiAlH_{0.35}$.

As in the case of crystal structure modification, the absolute amount of hydrogen in the unit cell itself does not affect the magnetic properties in a proportional way. In the case of TbNiAl-H, the removal of 50% of hydrogen completely recovers the magnetic phase transition characteristic for TbNiAl, whereas in GdNiAl-H the same change of the hydrogen content slightly changes the maximum value of susceptibility leaving the transition temperature unaffected. Such non-linear scaling of magnetic properties with H content points to the decisive role of the electronic density modification by hydrogen bonding, namely the decrease of the conduction electron concentration or the density of conduction electrons at the Fermi energy.

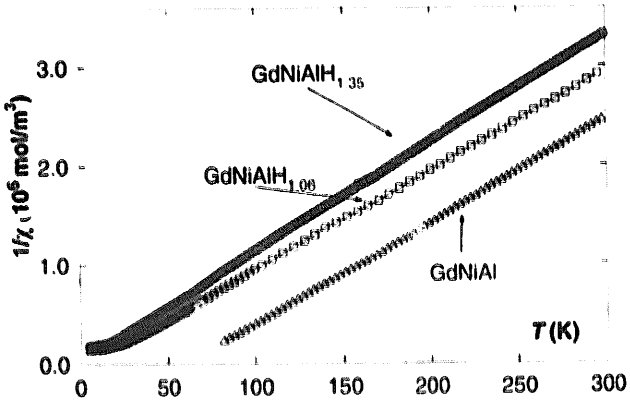

Fig. 5. Inverse susceptibility vs. temperature for GdNiAl-H system in the field of 1 T. The data for $GdNiAlH_{1.35}$ is shown using empty circles, for $GdNiAlH_{1.06}$ using empty squares and for GdNiAl using empty triangles.

The reduction of the strength of exchange interaction, which is quite a general feature of the *R*NiAl-H system is not, however, found in isoelectronic $NdNiInH_{1.7}$ [4]. NdNiIn is a ferromagnet with the ordering temperature $T_C = 20$ K [4], but after 1.7 H atoms f.u.$^{-1}$ have been incorporated into the crystal lattice it becomes antiferromagnet with a Néel temperature of 12 K [5], and shows a metamagnetic transition at about 2 T.

4. Conclusions

The general trend of weakening of magnetic interactions in presence of interstitial hydrogen can be traced in the *R*NiAl-H systems. This is reflected in the notable decrease of the ordering temperatures. The absolute value of the paramagnetic Curie temperature, which is proportional to the strength of exchange interaction, is also lowered with the increase of hydrogen content. It is possible to return gradually to the properties of parent *R*NiAl intermetallics by partial desorption of hydrogen, so that magnetic ordering takes place at the same temperatures. Although the presence of several tenths of H atoms per f.u. is sufficient for the weakening of magnetic interactions: $\chi(T)$ reaches maximal values much lower than corresponding *R*NiAl and Θ_p is also frequently several times smaller in hydrides. Thus, the modification of the electronic density resulting from the hydrogen incorporation into the lattice strongly affects magnetism, probably by decreasing the $N(E_F)$ value, thus reducing the number of conduction electrons, which mediate the RKKY interaction between the localised magnetic moments of 4f origin in rare-earth atoms.

In $RNiAlH_x$ lattices, hydrogen atoms presumably occupy several crystallographic positions with different binding energies, which is indicated by the vacuum decomposition spectra. Due to this, hydrogen can be removed from the crystal lattice in a step-wise manner, which provides a possibility of obtaining intermediate hydrides with lower hydrogen content, where H atoms can be removed only from particular crystallographic sites. The degree of orthorhombic deformation decreases with decrease of H content in the metal matrix and at a certain critical H concentration such distortion is suppressed with a return to the original hexagonal symmetry. The expansion of the unit cells taking place even for small amounts of hydrogen (≈ 10% of the maximal value) may indicate that the main mechanism of the crystal lattice distortion is the modification of DOS due to charge transfer between hydrogen and metal atoms.

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