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Hydrogen absorption–desorption, crystal structure and magnetism in RENiAl intermetallic compounds and their hydrides

A.V. Kolomiets[a,b,*], L. Havela[a], V.A. Yartys[b], A.V. Andreev[a,c]

[a]Department of Metal Physics, Charles University, Ke Karlovu 5, 121 16 Prague 2, Czech Republic
[b]Metal Hydrides Laboratory, Karpenko Physico–Mechanical Institute of the National Academy of Sciences of Ukraine, 5 Naukova Str., 290601 Lviv, Ukraine
[c]Institute of Physics, Academy of Sciences, Na Slovance 2, 180 00 Prague 8, Czech Republic

Abstract

At ambient pressures RENiAl (RE=Y, Gd, Tb, Dy, Er and Lu) ternary intermetallic compounds crystallising in the ZrNiAl type of crystal structure form hydrides containing up to 1.4 H/f.u. Hydrogenation leads to a drastic reduction of magnetic ordering temperatures. It is accompanied by changes of magnetic structures and, for the majority of compounds, by orthorhombic distortion of the initial hexagonal symmetry.

Keywords: Rare earth metals; Magnetism; Hydrides; Deuterides

1. Introduction

Intermetallic compounds of rare earth metals (RE) exhibit a vast variety of interesting physical properties among which magnetism attracts special attention. The main reason for such an interest is the fact, that magnetic order in these compounds is based on well defined magnetic moments of the 4f-origin. The 4f moments are coupled by indirect exchange interactions mediated by non-f electrons. Such interaction, which is always present in metallic systems with localised magnetic moments, is well accounted by the RKKY-model.

Aluminium additions to the composition of intermetallic compounds of rare earth and transition metals substantially influence their hydrogen sorption capacity and the stability of the hydrides formed. RE_3Ni_8Al [1] and $RE_3Ni_6Al_2$ [2] represent examples of such hydrogen absorbers with a rather high affinity to hydrogen.

Hydrogen interaction with RENiAl compounds was studied up to now for RE=Y only [3]. $YNiAlD_{1.45}$ deuteride was synthesised using gas pressure of 60 bar at a room temperature. Hydrogen absorption resulted in increase of the volume of the unit cell with no changes in its hexagonal symmetry [3].

In this paper we present experimental results concerning an influence of hydrogenation on magnetic properties of some RENiAl (RE=Y, Gd, Tb, Dy, Er and Lu) compounds, which crystallise in the hexagonal structure of the ZrNiAl type [4] and exhibit at low temperatures various types of antiferromagnetic and ferromagnetic ordering [5–9].

2. Experimental details

Intermetallic compounds RENiAl were prepared by arc melting of constituent metals in stoichiometric proportions. The alloys obtained were characterised by X-ray powder diffraction and found to be single phase materials with the crystal structures of the ZrNiAl type. The values of lattice parameters attained in this work are in good agreement with the literature data [5].

Hydrogenation (deuteration) was performed at hydrogen pressure of 1 bar. Initially the samples were activated in vacuo (1 Pa) at 300°C for 1 h. In most cases absorption started in 5–10 min after hydrogen admission into the reaction chamber. Usually a slow absorption rate was observed and about 70–90% of hydrogen was absorbed during the first 1–2 h of interaction. The quantity of absorbed gas was determined by monitoring the pressure drop in calibrated volume.

The structure of materials obtained by hydrogenation was studied using powder X-ray diffraction (Philips PW

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[*] Corresponding author. Tel.: +420-2-21911351; fax.: +420-2-21911351; e-mail: kolomiet@apollo.karlov.mff.cuni.cz

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1012/10 diffractometer with Cu-K_α radiation). These studies confirmed a completeness of hydrogenation since no peaks of the parent RENiAl compounds were found in the hydrogenated samples.

Magnetic properties were studied on randomly oriented powders, fixed by diluted glue, by means of Faraday balance and SQUID techniques. Faraday balance measurements were performed on the Oxford Instruments equipment at temperatures down to 1.8 K and fields up to 5 T. In several cases the Quantum Design SQUID magnetometer with the temperature range 1.7–400 K and available fields up to 5 T was used.

3. Results

Hydrogenation resulted in formation of hydrides containing 1–1.4 H atoms/f.u. RENiAl. For most of studied RENiAl compounds, namely for RE=Y, Gd, Tb, Dy, Ho and Er, hydrogenation (deuteration) caused an orthorhombic distortion of the original hexagonal unit cell accompanied by the relative increase of volume $\Delta V/V$ up to 6.6% (reached in the case of TbNiAl hydride). The development of lattice parameters with hydrogen absorption has a strong anisotropy. The expansion in the basal plane is accompanied by a contraction in the c-axis direction (up to 4.1% for RE=Tb). Certain anisotropy was found in the basal plane too, which leads to an orthorhombic distortion, which can be presented by parameter γ (see Table 1) and is in the range of 4.8–6.6%.

For RE=Tb two other hydrides have been obtained with a reduced hydrogen content. The first of them is characterised by orthorhombic symmetry [10] with much smaller distortion from hexagonality in comparison with that for saturated hydride. The third hydride phase, with the lowest hydrogen amount, as well as Lu-containing hydride preserved the initial hexagonal symmetry of the intermetallic compound.

Crystallographic parameters of initial intermetallic compounds and their hydrides are summarised in the Table 1.

Most detailed studies of hydrogen absorption–desorption properties were performed for a Tb-containing intermetallic compound.

Studies of hydrogen vacuum desorption indicated that hydrogen release from the TbNiAl saturated hydride already starts at room temperature and extends up to 400°C. Within low temperature range up to 200°C two overlapping peaks centred at 105°C and 160°C were observed. They are associated with the formation of two intermediate hydrides with the reduced hydrogen content comparing to the saturated $\mathrm{TbNiAlH}_{1.4}$, namely $\mathrm{TbNiAlH}_{0.7}$ and $\mathrm{TbNiAlH}_{0.4}$ hydrides. Magnetic properties of one of them (for hydrogenated sample with 0.7 H/TbNiAl) were studied in details. At higher temperature, i.e., at 320°C, the third effect of hydrogen desorption is observed in the HDTA spectrum, corresponding to a complete hydrogen release. A return to the lattice of intermetallic compound was confirmed by X-ray investigations after finishing the desorption.

Magnetic properties of the partially decomposed hydride (Fig. 1) resemble the behaviour of the parent compound. It orders antiferromagnetically at T_N~45 K, where a pronounced peak in $\chi(T)$ is found. Another, but much weaker maximum indicates additional magnetic phase transition at

Table 1
Crystallographic characteristics of parent RENiAl intermetallic compounds and their hydrides (deuterides)

Compound/hydride	a (Å)	b (Å)	c (Å)	$\Delta V/V$, %	$\Delta a/a$, %	$\Delta b/a\sqrt{3}$[a], %	γ[b], %	$\Delta c/c$, %
YNiAl	7.036(1)	−	3.839(1)					
$\mathrm{YNiAlH}_{1.2}$	7.602(4)	12.353(7)	3.713(4)	5.9	8.0	1.4	6.2	−3.3
GdNiAl	7.0125(8)		3.9140(9)					
$\mathrm{GdNiAlH}_{1.35}$	7.636(4)	12.378(1)	3.736(2)	5.9	8.9	1.9	6.4	−4.5
TbNiAl	6.999(1)	−	3.879(2)					
$\mathrm{TbNiAlH}_{0.4}$	7.034(1)	−	3.897(1)	1.5	0.5	−	−	0.5
$\mathrm{TbNiAlH}_{1.4}$ (saturated)	7.636(1)	12.353(2)	3.7209(7)	6.6	9.1	1.9	6.6	−4.1
$\mathrm{TbNiAlD}_{0.7}$ [c]	14.5195(5)[d]	12.4480(3)	3.8022(1)	4.4	3.7	2.7	1.0	−2.0
DyNiAl	6.9966(9)	−	3.847(1)					
$\mathrm{DyNiAlD}_{1.2}$	7.573(3)	12.340(6)	3.718(2)	6.5	8.2	1.8	5.9	−3.4
ErNiAl	6.970(2)	−	3.8003(6)					
$\mathrm{ErNiAlH}_{1.4}$	7.4804(3)	12.3298(5)	3.6888(2)	6.4	7.3	2.1	4.8	−2.9
LuNiAl	6.94392)	−	3.757(2)					
$\mathrm{LuNiAlH}_{1}$	7.192(3)	−	3.636(2)	3.8	3.6	−	−	−3.2

[a] $\Delta b/a\sqrt{3}$, where $\Delta b = b - a\cdot\sqrt{3}$ and a stands for lattice parameter of parent RENiAl compound, b stands for that in [010] direction of corresponding hydride (deuteride).

[b] $\gamma = (1 - b/\sqrt{3})/a$, where a and b stand for lattice parameters of hydride (deuteride).

[c] Ref. [10].

[d] Unit cell is doubled along [100] direction.

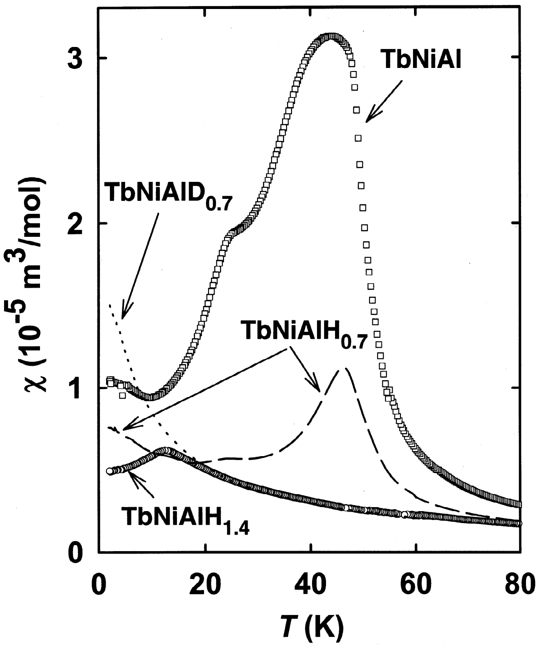

Fig. 1. Temperature dependence of magnetic susceptibility of TbNiAl and its hydrides and deuteride. All data were obtained in the field B=0.1 T except for the deuteride, where B=1 T was applied.

24 K. Temperatures of the magnetic phase transitions for TbNiAl are 48 K and 24 K, respectively. On the other hand, the shape of the anomalies connected with the transitions is rather different and the maximum susceptibility values are much smaller for the hydride. Effective moments evaluated from the $\chi(T)$ dependence are about 9.4 μ_B/f.u. in both cases, but the Θ_p values of the paramagnetic Curie temperature changed from about 25 K in TbNiAl to 8 K in the hydride. Similar to TbNiAl, related hydride displays a metamagnetic behaviour in rather weak magnetic fields below 1 T. All this is suggestive of similar magnetic structure in the hydride and pure TbNiAl, in which a complicated antiferromagnetic structure with moments along the c-axis was indicated by neutron diffraction [8,12,13].

On the other hand, the saturated hydride TbNiAlH$_{1.4}$ becomes antiferromagnetic at T_N=14.5 K (Fig. 1). The transition temperature shifts down with increasing field to about 10 K in B=3 T, but in contrast to the previous case no metamagnetism is observed in this field at T=4.2 K. The $\chi(T)$ dependence is influenced by the presence of a ferromagnetic impurity. An impurity elimination procedure leads to estimated Θ_p=−9 K. Surprisingly, no indications of magnetic transitions are found in TbNiAlD$_{0.7}$ (Fig. 1). $\chi(T)$ at higher temperatures is practically identical with TbNiAlH$_{1.4}$, but instead of maximum, a monotonous increase is observed down to the lowest temperatures. The χ-values in this range become field dependent. The estimate of effective magnetic moment from the Curie–Weiss behaviour above T=8 K gives 9.3 μ_B/Tb and Θ_P=−6.2 K. The field dependence of the magnetisation curves taken both at T=2 K and 4 K has no hysteresis and shows the tendency to saturation, which can be described by the Brillouin function if we assume the magnetic moment $\mu\approx6.5$ μ_B/f.u.

Magnetic susceptibility of GdNiAlH$_{1.3}$ (Fig. 2) obeys the Curie–Weiss law down to 20 K. At this temperature $\chi(T)$ turns abruptly upwards and a maximum is found at T=11 K in the field of 0.1 T. Application of a higher field leads to a suppression of the χ-values and the increase of χ with decreasing T becomes monotonous. This behaviour contrasts strongly with GdNiAl, which orders at T=59 K. The analysis of the high-temperature part of the susceptibility gives the effective moment of 7.7 μ_B/f.u. and Θ_P=−3.6 K. No anomalies are observed on the magnetisation curve, but due to a strong curvature at low fields it notably deviates from the Brillouin function.

ErNiAlH$_{1.4}$ behaves like a paramagnet with a Curie–Weiss behaviour at least down to 2 K (Fig. 3), with Brillouin-type magnetisation field dependence and magnetic moment of about 7 μ_B/f.u. The fitting of the paramagnetic susceptibility yields μ_{eff}=9.3 μ_B/f.u. and Θ_P=−3.6 K.

The susceptibility of DyNiAl-deuteride (Fig. 4) follows a Curie–Weiss law (μ_{eff}=10.3 μ_B/f.u., Θ_P=−8 K) down to 5 K. The maximum in $\chi(T)$, observed at T=5 K, points at antiferromagnetic transition. The field dependence of magnetisation at T=4.2 K does not show any hysteresis or metamagnetic transition up to B=5 T. The shape of the $M(B)$ curve, showing a trend to saturation, can be well accounted by a Brillouin function, supposing the moment of 8–9 μ_B/f.u.

Both intermetallics with non-magnetic rare-earths, YNiAlH$_{1.2}$ and LuNiAlH$_1$, exhibit temperature independent susceptibility followed by upturn at low temperatures.

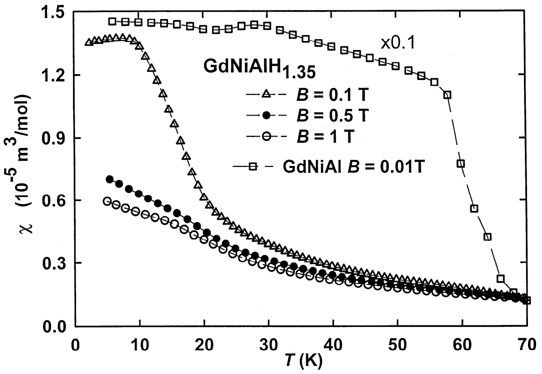

Fig. 2. Magnetic susceptibility of GdNiAlH$_{1.35}$ measured in various fields in comparison with the data obtained for GdNiAl intermetallic compound in very low fields (multiplied by the factor of 0.1 to fit in the same scale).

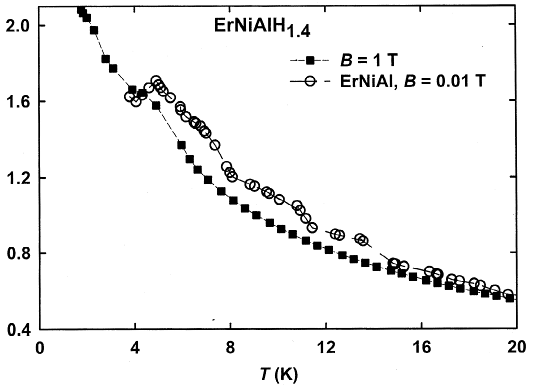

Fig. 3. Magnetic susceptibility of $ErNiAlH_{1.4}$ compared with the data obtained on ErNiAl.

This upturn can be explained as a result of admixture of magnetic rare-earths on the level of ~0.02 at. %. The hydrogen uptake yields the reduction of susceptibility down to χ_0~10^{-11} m^3/mol and χ_0~10^{-13} m^3/mol, respectively.

4. Discussion and conclusions

Comparing magnetic properties of RENiAl intermetallics with respective hydrides we see that hydrogenation significantly changes magnetic ordering temperatures and, most probably, the type of magnetic ordering. The latter statement can be deduced from reduced number of magnetic phase transitions and from qualitatively different types of related anomalies in hydrides and parent intermetallics. The strength of exchange interactions given by ordering temperatures is generally strongly reduced. Magnetic ordering temperatures follow approximately the De Gennes scaling in parent intermetallics. Thus in some cases, in which ordering temperatures are low in the parent intermetallics due to the small spin moment, it shifts out of the range achievable in our experiment ($ErNiAlH_{1.4}$). This trend can be connected with assumed effect of H-bonding and forming a low-lying s-band [11], which can lead to the reduction of the density of conduction electron states at the Fermi level $N(E_F)$. A fingerprint of such reduction can be seen also in the strong depression of susceptibility in Pauli paramagnets YNiAl and LuNiAl, which also reflects $N(E_F)$. Hydrogenation leads to a weakening of RE–RE exchange interaction, probably by reducing the density of states at E_F. Ni-3d states, which are effectively filled up in RENiAl compounds, probably remain ineffective for magnetism in hydrides, too.

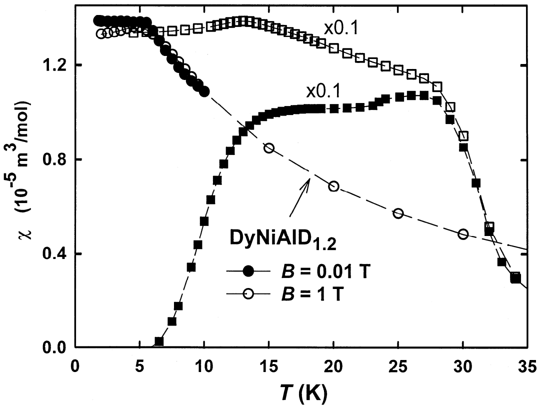

Fig. 4. Magnetic susceptibility of $DyNiAlD_{1.2}$ studied in the field $B=0.01$ T and 1 T (circles) compared with the data on DyNiAl obtained in $B=0.01$ T with zero-field cooling (full squares) and field cooling (empty squares). The latter two curves were adjusted by multiplying by the factor of 0.1.

The point which is less clear is the striking difference between the behaviour of Tb-containing saturated hydride and deuteride at low temperatures.

In conclusion we should note that most RENiAl compounds form hydrides with a H concentration between 1 and 1.4 H atoms per formula unit at ambient pressure.

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