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High field magnetization of metal hydrides under hydrogen pressure

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Abstract

The magnetization of the metal hydrides $GdFe_3H_x$ ($x=0$~3.6) and $Dy_6Fe_{23}H_x$ ($x=0$~20.3) was measured in magnetic fields up to 29 T at 77 K. For these measurements the hydrides were prepared in situ in a glass holder with gradually varying hydride composition x at room temperature. For each system the magnetization curve varied systematically with hydrogen content. The dependence of magnetization on hydrogen content is discussed.

Keywords: Magnetic properties; R–Fe compounds; high field magnetization; $GdFe_3H_x$; $Dy_6Fe_{23}H_x$

1. Introduction

A large number of investigations have shown that absorption of hydrogen remarkably influences the magnetic properties of the R–T intermetallic compounds which are formed between rare earth R and transition metals T [1]. Conversely, we can obtain information on hydride phases from their magnetic behavior [2,3]. For the $LaCo_5H_x$ system, for example, the magnetization M decreases linearly with hydrogen content x in the $\alpha-\beta$ and the $\beta-\gamma$ regions but the gradient dM/dx differs between the two regions [2]. In general, the magnetization varies linearly with hydrogen content in the two phase region because the magnetization is the weighted average of the magnetic moment between the two hydride phases.

The R–T intermetallic compounds and their hydrides often have a large magnetocrystalline anisotropy with anisotropy fields higher than several tesla. In such a case, neither the saturation magnetization nor the spontaneous magnetization can be determined exactly from powder magnetization in low fields. This difficulty may be resolved by applying high fields in magnetization measurements.

If the equilibrium hydrogen pressure is very low, as in the case of R–Fe based hydrides, it is difficult to determine the hydride phases from the pressure composition isotherm (PCT) measurement at ordinary temperatures. Hence, the magnetization measurement accompanied with in situ preparation of hydrides can yield useful information on the hydride phases. The in situ method is also required for unstable hydrides which form at higher pressures.

In this paper we describe the experimental system for a high field magnetization measurement which includes in situ preparation of the hydrides as applied to $GdFe_3H_x$ and $Dy_6Fe_{23}H_x$.

The compound $GdFe_3$ is a ferrimagnet crystallizing with the $PuNi_3$-structure type. Absorption of hydrogen leads to a weakening in the exchange coupling n_{RT} between the rare earth moment M_R and the Fe moment M_T. As a result, the compensation temperature T_{comp} for ferrimagnetism is decreased: $T_{comp}=280$ K for $x=1.5$ and $T_{comp}=161$ K for $x=3.0$ [4]. The PCT relation for the system $GdFe_3$–H was measured at temperatures above 150 °C by Bechman et al. [5]. Two hydride phases appear in the PCT: The α phase exists in the region of $x<0.6$ and the β phase extends from $x=1.4$ to 3.1.

The compound Dy_6Fe_{23} is also a ferrimagnetic which crystallizes with the Th_6Mn_{23}-structure type. Matsuda et al. [4] reported that in the hydrides $Dy_6Fe_{23}H_x$ a fanning of the Dy moments occurs in the ground state, resulting in a decrease in the net Dy moment. The compensation temperature T_{temp} decreases with increasing hydrogen contents: $T_{comp}=265$ K for $x=12$ and 186 K for $x=18$. This behavior is attributed to the weakening of n_{RT} upon absorption of hydrogen. The PCT relation has not been

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reported for the system Dy_6Fe_{23}–H probably because of very low equilibrium pressure.

2. Experimental

The starting compounds were prepared by argon arc-melting of the constituent metals. This purity was 99.99% for Fe and 99.9% for Gd and Dy. The ingots were annealed at 1200 K for 24 h under a continuous flow of purified argon for homogenization. Powder X-ray diffraction profiles showed that they were single phase and had the desired crystal structures.

Fig. 1 illustrates the experimental system and the sample holder. The latter was a Pyrex glass tube with an inside diameter of about 3.3 mm. The maximum working pressure was 0.3 MPa. The sample with a weight of 0.4~0.5 g was introduced into the glass tube and fixed by compacted silica wool in order to prevent it from moving in the magnetic fields. The sample holder was connected via a 1/4 inch stainless steel tube to a PCT unit by which the hydrogen content in the sample was determined using the volumetric method. After hydrogenation, the sample holder was inserted into the center of the magnet.

Pulsed magnetic fields were produced by capacitor discharge using a so-called ice magnet, which was reinforced by ice when the magnet was cooled with liquid nitrogen. The maximum magnetic field was 29 T and the pulse width was 5 ms at a charging voltage of 5000 V with a capacitor bank of 2.4 mF. The magnetization was measured by the induction method at 77 K. This temperature was much lower than the Curie temperature and the compensation temperature for $GdFe_3H_x$ and $Dy_6Fe_{23}H_x$.

The experimental procedure was as follows: First, the magnetization of the starting metal sample was measured at 77 K. Then, the sample was evacuated at 600 K for 3 h for activation. After activation the sample was reacted with hydrogen to a given composition at 300 K. The magnetization of this hydride sample was measured again at 77 K. In the next step, a hydride with a larger hydrogen content was prepared at 300 K. This cycle was repeated until the applied hydrogen pressure reached the maximum working pressure of the glass tube. Each hydride was formed in the absorbing process only. Because these hydrides have a rather low equilibrium pressure, it was difficult to control the hydrogen content in the desorbing process. The hydrogen composition was taken to be $x=0.5$, 1.0, 2.0, 2.5, 3.0, 3.4, 3.6 for $GdFe_3H_x$ and $x=2.9$, 5.7, 8.4, 9.9, 11.7, 12.7, 14.4, 16.0, 17.4, 19.0, 20.3 for $Dy_6Fe_{23}H_x$.

3. Results and discussion

Fig. 2 and Fig. 3 present the magnetization curves at 77 K for $GdFe_3H_x$ ($x=0$~3.6) and $Dy_6Fe_{23}H_x$ ($x=0$~20.3), respectively. Although the spin-flip transition from the collinear to the non-collinear spin structure occurs at 4.2 K in magnetic fields lower than 39 T in both the hydrides [4], no clear transitions appear at 77 K up to 29 T.

Fig. 4 shows the dependence of the spontaneous magnetization on the hydrogen composition for $GdFe_3H_x$. Here, the spontaneous magnetization is obtained by extrapolating the magnetization linearly from high fields of several tesla to zero field because YFe_3, a related compounds of $GdFe_3$, has the anisotropic field of $B_a=4$ T and its hydride $YFe_3H_{1.8}$ has $B_a=3$ T [6]. Included in the figure is the absorption hydrogen pressure at 25 °C as determined by the present experiment and the desorption pressure at 150 °C given in Refs. [5]. The spontaneous magnetization shows a minimum at $x=1.5$. Obviously, the composition $x=1.5$ corresponds to the lower end of the β

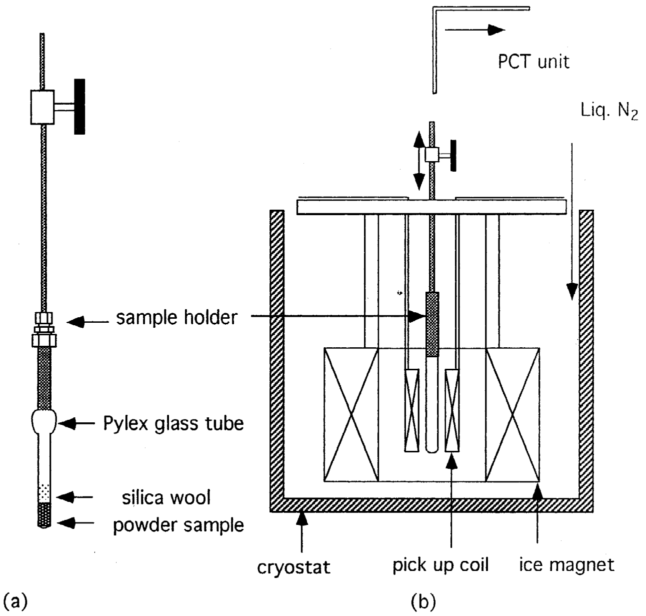

Fig. 1. (a) Sample holder, (b) Experimental system.

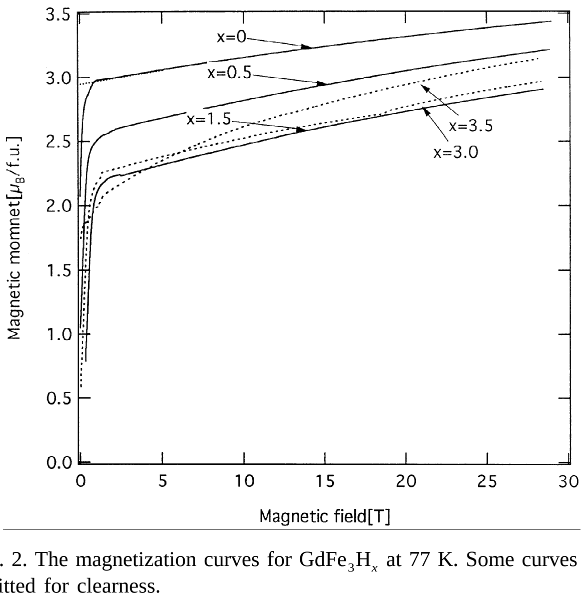

Fig. 2. The magnetization curves for $GdFe_3H_x$ at 77 K. Some curves are omitted for clearness.

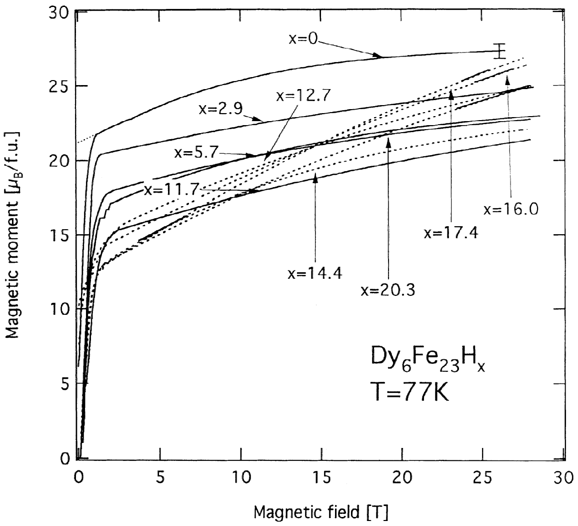

Fig. 3. The magnetization curves for $Dy_6Fe_{23}H_x$ at 77 K. Some curves are omitted for clearness.

phase, which can be recognized in the pressure curves at 25 °C and 150 °C. The magnetization in the α–β region ($0.5<x<1.5$) decreases linearly with increasing hydrogen content because of the weighted average of the magnetic moment between the α and β phases. In the higher composition region $x>1.5$, there is only the β phase in the PCT diagram at 150 °C, but the magnetization varies in a complicated manner.

Fig. 5 shows the dependence of the spontaneous magnetization on hydrogen composition for $Dy_6Fe_{23}H_x$. The hydrogen pressures after the completion of absorption at 25 °C are also plotted although they do not correspond to the equilibrium pressure. The absorption pressure increases around $x=8.4\sim9.9$ and $x=14.4\sim16.0$. In addition, the gradient dM/dx changes around $x\simeq5.7$, 9.9 and 14.4.

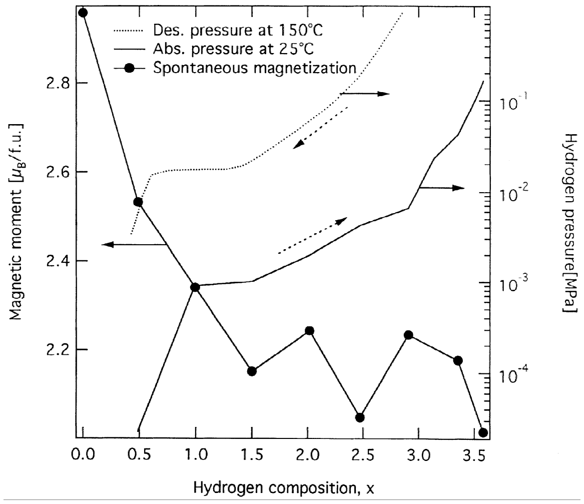

Fig. 4. Dependence of spontaneous magnetization on hydrogen constant for $GdFe_3H_x$. The full and dotted curves denote the hydrogen pressures in the absorption process at 25 °C and the desorption process at 150 °C, respectively.

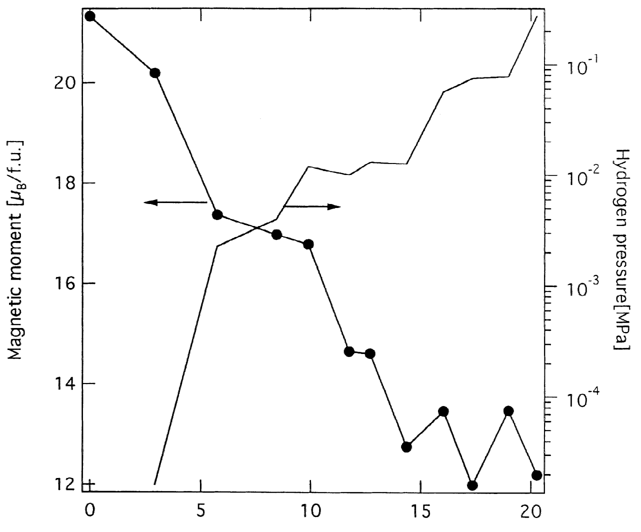

Fig. 5. Dependence of the spontaneous magnetization on the hydrogen composition for $Dy_6Fe_{23}H_x$. The full curve denotes the absorption pressure at 25 °C.

For the systems Er_6Fe_{23}–H and Ho_6Fe_{23}–H [7,8], three hydride phases were observed in PCT diagrams: the γ phase at $x\approx8$, the δ phase at $x\approx12$ and the ε phase for $x>12$. Judging from the isostructural compounds R_6Fe_{23} (R=Dy, Er, Ho) we presume that the hydride phases in $Dy_6Fe_{23}H_x$ exist around $x\simeq5.7$ (β phase), 9.9 (γ phase) and 14.4 (δ phase).

In summary, the magnetization of the metal hydrides $Dy_4Fe_{23}H_x$ and $GdFe_3H_x$ was measured in magnetic fields up to 29 T at 77 K for various exactly determined hydrogen compositions. The magnetic behavior was correlated to these hydride phases. For the $GdFe_3H_x$ system, the β phase starts at $x=1.5$. For the $Dy_6Fe_{23}H_x$ system, hydride phases were presumed to exist around $x\simeq5.7$ (β phase), $x\simeq9.9$ (γ phase) and $x\simeq14.4$ (δ phase).

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