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Inversion of the magnetization near the compensation point in $TbFe_2H_x$ hydrides

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Abstract

The temperature dependences of the magnetization and coercive force H_c were studied in $TbFe_2H_x$ and $Tb_{0.8}Y_{0.2}Fe_2H_x$ hydrides with different values of x. At $x \geqslant 3.9$ the hydrides were found to have a compensation temperature θ_c, near which H_c had a maximum and reaches 0.46 MA m^{-1}. Shifted hysteresis loops were observed after cooling the samples from $T > \theta_c$ to $T < \theta_c$. If the cooling was carried out in a magnetic field with $H < H_c$, the magnetization changes its sign near θ_c. An inversional permanent magnet was prepared on the basis of $TbFe_2H_{4.0}$ hydride. The remanent magnetization of this magnet changes from +5 A m^2 kg^{-1} at 250 K to −15 A m^2 kg^{-1} at 77 K.

1. Introduction

The cubic intermetallic RFe_2 compounds (where R is a rare earth element) are known to absorb hydrogen actively at room temperature and form stable hydrides of approximate composition RFe_2H_4 [1, 2]. In parent heavy rare earth compounds ($R \equiv Gd$, ..., Tm), rare earth and Fe magnetic moments are ferrimagnetically ordered. In the case of $R \equiv Er$ and Tm, the RFe_2 compounds have compensation temperatures of $\theta_c = 490$ and $\theta_c = 240$ K respectively [3, 4].

Hydrogenation of RFe_2 compounds, as a rule, leads to a decrease in the Curie temperature T_C (except for $CeFe_2$ [5, 6]), which indicates a weakening of the Fe–Fe exchange interaction. The magnetic moment of Fe increases on the introduction of hydrogen, whereas the R moment decreases [7, 8]. Such a change in sublattice magnetic moments together with the weakening of the R–Fe exchange interaction leads to a shift of θ_c towards lower temperatures for $R \equiv Er$ and Tm, and to the appearance of θ_c in the compounds with $R \equiv Gd$, Dy, Ho [7, 9–11]. In ref. 12, it was shown that no compensation temperature θ_c is observed in $TbFe_2H_x$ hydrides up to $x = 3.47$.

In the present paper, we report on the investigation of the temperature dependences of the magnetization and coercive force H_c in $TbFe_2H_x$ hydrides with different x values. It is shown that the $TbFe_2H_{4.0}$ hydride has a compensation point and can be considered as an inversional permanent magnet, *i.e.* a magnet which changes the sign of its remanent magnetization during cooling from $T > \theta_c$ to $T < \theta_c$.

2. Experimental details

The alloys investigated were prepared by melting the constituents in an induction furnace and additional annealing for 50 h at 1000 °C. X-ray phase analysis showed that the amount of additional phases in the samples was no more than 3%. Before hydrogenation the surface of the samples was activated by heating to 200 °C *in vacuo* (10^{-5} Torr).

Hydrogenation was carried out by a purified hydrogen gas obtained by the decomposition of $LaNi_5H_x$ hydride. The samples interacted with the hydrogen during 0.5 h at a hydrogen pressure of about 0.2 MPa. To obtain the hydrides with different hydrogen contents, the temperature of hydrogenation varied from 20 to 130 °C. As a rule, the samples obtained consisted of a mixture of two or more phases with approximately the same lattice parameters. The composition, temperature of hydrogenation (T_h) and lattice parameters obtained for the samples are listed in Table 1.

The hydrogen content was determined from the change in the sample mass. In the process of hydrogenation, the ingots were pulverized into a powder of particles with mean size 30–100 μm. These powders were pressed into pellets 5 mm in diameter and 1.5 mm thick under a pressure of 5×10^8 Pa.

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TABLE 1. Composition, temperature of hydrogenation (T_h) and lattice parameters of samples investigated

Composition	T_h (°C)	Main phase				Additional phase	
		Structure	Lattice parameters		Vol.%	Structure	Lattice parameter a (nm)
			a (nm)	α (deg.)			
$TbFe_2$	–	f.c.c.	0.7356	–	100		
$TbFe_2H_{1.60}$	130	f.c.c.	0.7884	–	100		
$TbFe_2H_{3.56}$	60	Rhombohedr.	0.7936	91.08	80	f.c.c.	0.7950
$TbFe_2H_{3.90}$	45	f.c.c.	0.7960	–	80	f.c.c.	0.7979
$TbFe_2H_{4.00}$	20	f.c.c.	0.7984	–	100		
$Tb_{0.8}Y_{0.2}Fe_2$	–	f.c.c.		–	100		
$Tb_{0.8}Y_{0.2}Fe_2H_{3.9}$	20	Rhombohedr.	0.7988	92.18	70	f.c.c.	0.7968

The magnetic measurements were carried out using a vibrating sample magnetometer in magnetic fields up to 1.6 MA m^{-1}.

3. Results and discussion

Figure 1 shows the temperature dependences of magnetization of $TbFe_2H_x$ hydrides with $0 \leqslant x \leqslant 4$ in a magnetic field of 0.5 MA m^{-1}. It can be seen that the Curie temperature decreases with increasing x, which indicates a weakening of the Fe–Fe exchange interaction as a result of the increase in interatomic distances between the Fe ions (see Table 1). At $x \geqslant 3.9$, the temperature dependences of the magnetization have a minimum which is shifted to lower temperatures with increasing x. This minimum can be connected with the appearance of a compensation point θ_c. However, at the minimum points, there is a non-zero magnetization obtained by extrapolation to the zero field from the high field region. In addition, X-ray investigation showed that, even in the case of single-phase samples, the X-ray reflections in hydrides are broader than those for the parent alloy. Hence, it can be concluded that the hydrided samples consist of grains with different θ_c values, because of the heterogeneous distribution of hydrogen.

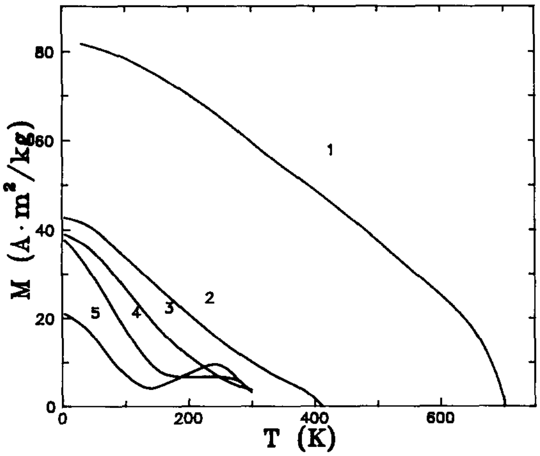

Fig. 1. The temperature dependences of the magnetization in a field $H = 0.5$ MA m^{-1} of $TbFe_2H_x$ hydrides with different values of x: (1) $x = 0$; (2) $x = 1.6$; (3) $x = 3.56$; (4) $x = 3.9$; (5) $x = 4.0$.

Ferrimagnetics usually have a sharp maximum of H_c near θ_c, since for any coercive force model $H_c \sim 1/M_s$, whereas $M_s \rightarrow 0$ at $T \rightarrow \theta_c$. Figure 2 shows the temperature dependence of H_c of the $TbFe_2H_{4.0}$ sample. It is seen that the $H_c(T)$ curve has only a weak maximum around θ_c. This can be connected both with the heterogeneous distribution of hydrogen in the sample and with the increase in H_c owing to the increase in the magnetocrystalline anisotropy constant when the temperature decreases.

The high H_c values near θ_c cause the inversion of the magnetization in this compound. Actually, at $\theta_c < T < T_C$, when the sample is placed in a magnetic field the magnetic moment of Fe exceeds that of Tb and is oriented along the field direction. When the sample is cooled to $T < \theta_c$, the total magnetic moment

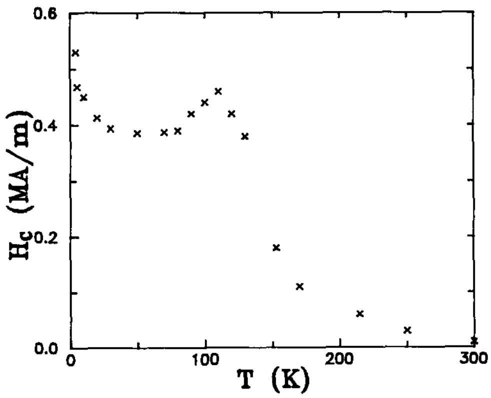

Fig. 2. The temperature dependence of the coercive force H_c of the $TbFe_2H_{4.0}$ sample.

seems to be parallel to the Tb sublattice moment. If the applied field is less than H_c, there is no rotation of the sublattice magnetic moments and the total magnetization changes its sign near θ_c.

The inversion of the magnetization is observed in $TbFe_2H_{4.0}$ both upon heating (Fig. 3, curve 1) and cooling (Fig. 3, curve 2) of the sample in a magnetic field less than 0.4 MA m^{-1}, the latter value correlates well with the H_c value at θ_c.

The temperature of magnetization inversion depends on the initial magnetic state, because the applied magnetic field is insufficient to magnetize the sample to saturation. This is why the temperatures of magnetization inversion from curves 1 and 2 (Fig. 3) are slightly different. It should be noticed that curve 2 is reversible from 4.2 K to T_C while curve 1 is reversible only to the temperature which exceeds slightly the compensation temperature.

The inversion of magnetization leads to the appearance of shifted hysteresis loops in the sample at $T<\theta_c$ (Fig. 4). The shape of the hysteresis loops allows us to suppose that the sample contains highly coercive particles with $H_c>1.6$ MA m^{-1}. These particles have a negative magnetization after cooling the sample to $T<\theta_c$, because the applied field cannot remagnetize them. Hence, they will give a negative contribution to the total magnetization and shift the hysteresis loop against the applied field direction (*i.e.* downwards in Fig. 4).

The change in sign of the magnetization near θ_c was discovered first in $ErFe_2$ [13]. Later, on the basis of this phenomenon, a new type of inversional permanent magnet was developed using $TmCo_3$ and Tm_2Co_7 intermetallics [14] that can be used as temperature indicators, switchers etc.

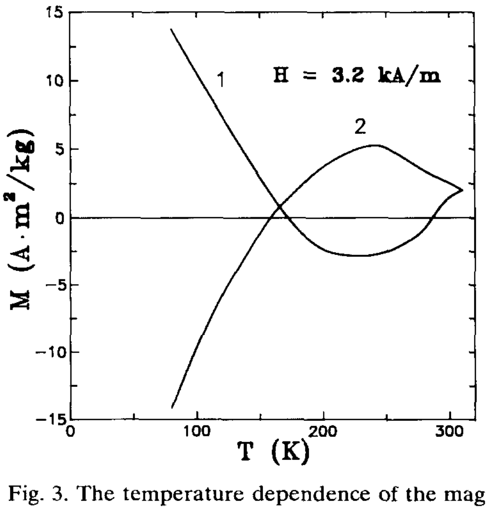

Fig. 3. The temperature dependence of the magnetization of the $TbFe_2H_{4.0}$ sample in a magnetic field of 3.2 kA m^{-1}: (1) heating after sample was magnetized in a field 1.6 MA m^{-1} at 4.2 K; (2) cooling.

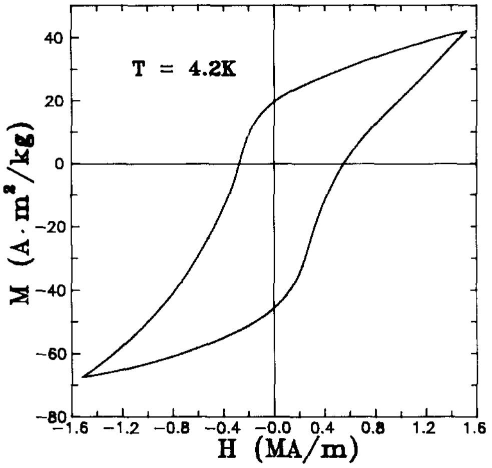

Fig. 4. Shifted hysteresis loop of $TbFe_2H_{4.0}$ sample measured after cooling from 300 to 4.2 K in a field $H=3.2$ kA m^{-1}.

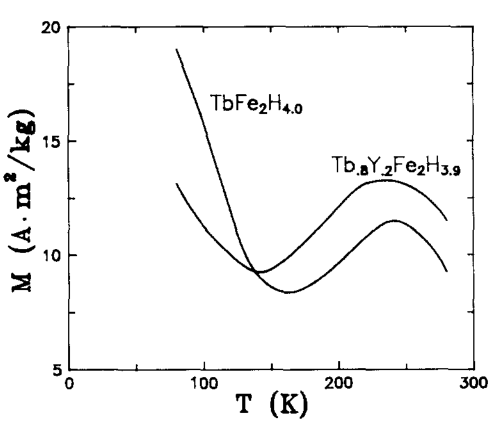

Fig. 5. The temperature dependences of the magnetization of $TbFe_2H_{4.0}$ and $Tb_{0.8}Y_{0.2}Fe_2H_{3.9}$ samples in a field $H=1$ MA m^{-1}.

We prepared magnets on the basis of $TbFe_2H_{4.0}$ hydride by isotropic pressing of pulverized hydride powder without any additional treatment. Even at room temperature these magnets have a sufficient coercive force not to allow them to be demagnetized by their own internal field. This feature distinguishes $TbFe_2H_{4.0}$ hydride from the other compositions ($TmCo_3$, Tm_2Co_7) from which the inversional permanent magnets are prepared using standard metalloceramic technology [14].

It is seen from Fig. 1 that θ_c can be shifted towards higher temperatures by decreasing the hydrogen content in the sample. On the other hand, θ_c can be decreased by replacing some of the Tb atoms by non-magnetic atoms, *e.g.* Y. Figure 5 shows that $Tb_{0.8}Y_{0.2}Fe_2H_{3.9}$ hydride has a lower θ_c value than that of $TbFe_2H_{4.0}$. Since addition of Y leads to a decrease in the magnetic moment of the R sublattice, the magnetization of Y-containing hydride became smaller at $T<\theta_c$ and higher at $T>\theta_c$.

Finally, Table 2 summarizes some magnetic characteristics of the hydrides investigated, that are useful for practical application as inversional permanent mag-

TABLE 2. Comparison of magnetic characteristics of $TbFe_2H_{4.0}$ and $Tb_{0.8}Y_{0.2}Fe_2H_{3.9}$ samples and inversional permanent magnets on the basis of $TmCo_3$ and Tm_2Co_7 compounds [14]

Composition	θ_c (K)	$4\pi M_r$ (mT)		H_c (kA m^{-1})	
		77 K	250 K	77 K	250 K
$TbFe_2H_{4.0}$	160	−13.4	+4.5	384	18
$Tb_{0.8}Y_{0.2}Fe_2H_{3.9}$	140	−10.3	+5.4	420	36
$TmCo_3$	120	−12.3	+23.4	480	<8
Tm_2Co_7	90	−3.8	+35.8	600	<8

nets. Also, this table contains the characteristics of inversional magnets on the basis of $TmCo_3$ and Tm_2Co_7 [14]. In spite of the fact that $TbFe_2H_x$ hydrides have slightly worse characteristics than those of Tm–Co magnets, their sufficiently high H_c at room temperature, simplicity of preparation and possibility to change θ_c reversibly by variation of hydrogen content make these hydrides suitable materials for inversional permanent magnets.

4. Conclusions

The introduction of hydrogen into $TbFe_2$ intermetallic compounds leads to the appearance of compensation temperatures θ_c. In $TbFe_2H_{4.0}$, $\theta_c = 160$ K. However, the samples have a non-zero magnetization at $T = \theta_c$, that indicates a heterogeneous distribution of hydrogen in the sample.

The reversible inversion of magnetization near θ_c was found in $TbFe_2H_x$ compounds, which makes these materials suitable for the creation of inversional permanent magnets. Having sufficiently high coercive force, the aforementioned magnets can be prepared by simple isotropic pressing of pulverized hydride powder.

It is shown that the magnetic characteristics of inversional permanent magnets of $TbFe_2H_x$, such as the magnetization coercive force and temperature of inversion of magnetization, can be changed over wide ranges both by changing x and by substituting some of the Tb ions with non-magnetic ions, *e.g.* Y.

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