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About hydrogen insertion in $ThMn_{12}$ type alloys

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Abstract

The absorption of hydrogen in ternary $RFe_{12-x}M_x$ (R=Y or rare earth, M=Ti, Mo) alloys has been investigated by neutron diffraction. These compounds crystallise in the tetragonal (I4/mmm) structure of $ThMn_{12}$ type. In this work we report structural and magnetic investigations undertaken by neutron diffraction for some hydrides with high hydrogen contents and we focus on the location of hydrogen in Ti and Mo containing materials. The effects of hydrogenation on the intrinsic properties such as enhancement of Curie temperature, lattice parameters, Fe moment as determined by neutron diffraction, magnetic and Mössbauer measurements, are discussed.

Keywords: Neutron diffraction; Crystal structure; Magnetic structure; Hydrogen absorption

1. Introduction

The search for permanent magnet materials has led to the discovery of ternary Fe-rich rare earth intermetallic compounds of type $RFe_{12-x}M_x$ (R=rare earth or Yttrium, and M=transition metal element) [1–4]. This series of alloys stabilises with the $ThMn_{12}$ type crystal structure (space group I4/mmm) [5]. For selected R and M elements, x (substituent) and y (interstitial) contents, potentially hard magnetic properties are achieved in $R Fe_{12-x}M_xX_y$ (X=H, C, N) [6,7]. It has been admitted that y is strictly less than 1 namely for X=C, N; the corresponding interstitial site occupied by X=H is the 2R-4Fe octahedron. However, $RFe_{12-x}M_xH_y$ hydrides have been synthesised with higher content $1<y<2$ [6–8] indicating that other interstitial sites must be accounted for in the hydrogen uptake process.

2. Experimental procedures

All the samples were prepared by induction melting of stoichiometric amounts of constituent elements (99.9% or better, purity) in the water-cooled copper crucible, under an atmosphere of very pure argon. The compounds were melted several times to insure homogeneity. Hydrogenation was performed in a steel autoclave, by using moderate hydrogen gas pressure ranges (10^5–10^6Pa).

Various samples $HoFe_{11}TiH_{x=0,\ 1.8}$, $YFe_{11}TiH_{x=0,\ 0.8,\ 1.9}$ and $YFe_{10}Mo_2H_{1.3}$ were studied by powder neutron diffraction technique at low and/or room temperature, using, the diffractometers D2B/D1B installed in the Institute Laue-Langevin, Grenoble.

Magnetisation and A.C magnetic susceptibility measurements for $YFe_{11}TiHx$ (x=0, 0.9), were performed on samples that had been previously oriented under a magnetic field and then glued. Non-oriented samples were also used for the measurements from 4 to 300 K and under fields of up to 5 T. Finally, ^{57}Fe Mössbauer spectroscopy measurements were performed at low temperature on $YFe_{11}TiH_x$ (x=0, 1.9).

3. Results and discussion

The X-ray diffraction patterns obtained for different compounds before and after hydrogenation exhibit lines characteristic of the body-centred tetragonal $ThMn_{12}$ type crystal structure. Insertion of hydrogen leads to an increase in lattice parameters and a change in the unit cell volume, as listed in the Table 1. It has been shown that in these hydrides ($RFe_{12-x}M_xH_y$), when the contents of hydrogen y is strictly less than one, the H atoms occupy the 2b sites coordinated by an octahedron 2R-4Fe. The neutron diffraction refinements with $y>1$ for $YFe_{11}TiH_{1.9}$, $YFe_{10}Mo_2H_{1.3}$ and $HoFe_{11}TiH_{1.8}$ demonstrate that the hydrogen atoms fully fill the 2b sites and partially the 8h sites. The 8h sites are triangular bipyramids defined as 1R(2a),2(Fe-M)8i,2Fe8f. Considering the refined atom positions, the

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Table 1
Unit cell parameters and volume for $RFe_{12-x}M_x$ and their hydrides (R=Y, Ho and M=Ti, Mo)

	a (Å)	c (Å)	$\Delta a/a \cdot 10^3$	$\Delta c/c \cdot 10^3$	c/a	V (Å^3)	$\Delta V/V \cdot 10^2$
$YFe_{11}Ti$	8.4797 (4)	4.7713 (2)	–	–	0.5627	343.08	–
$YFe_{11}TiH_{0.8}$	8.5146 (5)	4.7830 (3)	4.12	2.45	0.5617	346.76	1.07
$YFe_{11}TiH_{1.8}$	8.5167 (2)	4.7890 (3)	4.36	3.71	0.5623	347.37	1.25
$HoFe_{11}Ti$	8.4946 (3)	4.7862 (3)	–	–	0.5634	345.36	–
$HoFe_{11}TiH_{1.8}$	8.5260 (7)	4.7954 (4)	3.70	1.92	0.5624	348.59	0.94
$YFe_{10.5}Mo_{1.5}$	8.527 (3)	4.784 (1)	–	–	0.5610	347.84	-
$YFe_{10.5}Mo_{1.5}H_{0.9}$	8.558 (2)	4.797 (2)	3.64	2.72	0.5605	351.33	1.00
$HoFe_{10.5}Mo_{1.5}$	8.518 (3)	4.786 (1)	–	–	0.5619	347.26	–
$HoFe_{10.5}Mo_{1.5}H_{0.9}$	8.545 (3)	4.788 (1)	3.17	0.42	0.5603	349.61	0.78
$HoFe_{11}Mo$	8.498 (1)	4.773 (1)	–	–	0.5617	344.79	–
$HoFe_{11}MoH_{1.3}$	8.524 (2)	4.784 (1)	3.05	2.30	0.5612	347.60	0.82
$HoFe_{10}Mo_2$	8.537 (1)	4.7897 (8)	–	–	0.5611	349.08	–
$HoFe_{10}Mo_2H_{1.8}$	8.575 (1)	4.7975 (8)	4.45	1.63	0.5595	352.76	1.05

corresponding insertion sphere radius could appear somewhat small. However the latter should be locally larger when two M atoms are present, and for that reason should also be far more attractive in terms of electronegativity difference. From a simple distribution analysis of the M atoms, it appears that statistically 0.8125/*fu* of these (R-2M-2Fe) sites can be accessible to hydrogen insertion, taking into account that two neighbouring bipyramids are at least separated by 2.75 Å (i.e., simultaneously occupied). Thus a final limit of $y \cong 1.8$ H/fu, experimentally determined [6,8] appears to be reasonable. The refinement results, including coordinates of crystallographic sites, occupation numbers in these sites, thermal coefficients and atomic magnetic moments for $HoFe_{11}Ti$ and $HoFe_{11}H_{1,8}$ at 4.2 and 300 K, are presented in Table 2 and Table 3.

As in other studies by magnetisation measurements of the spin reorientation in $HoFe_{11}Ti$ [9,10], analysis of powder patterns confirm that the low temperature (4.2 K) magnetic structure is non axial. The resulting easy axis deviates from the $\vec{c}$ direction, not only for the pure compound but also for the hydride. As with the magnetic structure of $Ho_2Fe_{14}BH_x$ system determined from the neutron powder investigations, we notice the same effects of hydrogen absorption: the higher the hydrogen content, the higher the deviation of magnetisation from the axis. At 4.2 K it is 11× for $HoFe_{11}Ti$ and 33× for $HoFe_{11}H_{1,8}$.

Table 2
Crystal and magnetic neutron data of $HoFe_{11}Ti$ at 4.2 and 300 K

	x	y	z	B_{iso}	N_{oc}	$\mu(\mu_B)$	$\theta(\infty)$	$\phi(\infty)$	T(K)
Ho-2a	0	0	0	1.19 (24)		9.43 (27)	169 (2)	45	4.2
	0	0	0	1.31 (22)	0.0625	5.01 (20)	0	0	300
Fe1-Ti-8i	0.3599 (9)	0	0	0.21 (16)	0.5	2.13 (18)	11 (2)	225	4.2
	0.3575 (5)	0	0	0.78 (14)	0.5	1.55 (14)	0	0	300
Fe2-8j	0.2750 (9)	0.5	0	0.11 (10)	0.5	1.99 (17)	11 (2)	225	4.2
	0.2751 (9)	0.5	0	0.65 (7)	0.5	1.67 (15)	0	0	300
Fe3-8f	0.25	0.25	0.25	0.12 (11)	0.5	1.87 (13)	11 (2)	225	4.2
	0.25	0.25	0.25	0.59 (7)	0.5	1.54 (09)	0	0	300

Table 3
Crystal and magnetic neutron data of $HoFe_{11}TiH_{1.8}$ at 4.2 and 300 K

	x	y	z	B_{iso}	N_{oc}	$m(m_B)$	$q(\infty)$	$f(\infty)$	T(K)
Ho-2a	0	0	0	2.31 (35)		8.80 (30)	147 (2)	45	4.2
	0	0	0	1.05 (17)	0.0625	4.16 (19)	0	0	300
Fe1-Ti-8i	0.3584 (4)	0	0	0.55 (8)	0.5	1.75 (19)	33 (2)	225	4.2
	0.3584 (4)	0	0	0.80 (9)	0.5	2.15 (25)	0	0	300
Fe2-8j	0.2750 (9)	0.5	0	0.48 (8)	0.5	2.19 (16)	33 (2)	225	4.2
	0.2738 (5)	0.5	0	0.14 (8)	0.5	2.18 (16)	0	0	300
Fe3-8f	0.25	0.25	0.25	0.59 (5)	0.5	1.06 (06)	33 (2)	225	4.2
	0.25	0.25	0.25	0.10 (8)	0.5	2.04 (11)	0	0	300
H1-2b	0.5	0.5	0	2.36 (6)		–	–	–	4.2
	0.5	0.50	0	1.10 (4)	0.0625	–	–	–	300
H1-8h	0.164 (18)	0.164(18)	0	2.36 (6)	0.025	–	–	–	4.2
	0.172 (8)	0.172(8)	0	1.10 (4)		–	–	–	300

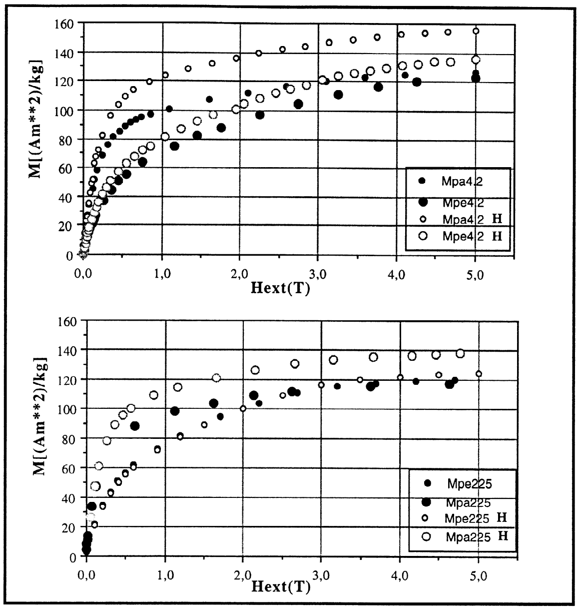

Fig. 1. Magnetisation curves of $YFe_{11}TiH_x$ ($x=0$, 0.8) at 4.2 and 300 K in the directions parallel (Mpa) and perpendicular (Mpe) to the aligned direction.

But at room temperature the magnetic structure is found to be collinear with the c-axis.

The field dependence of magnetisation, measured parallel and perpendicular to the aligned direction of oriented powders of the $YFe_{11}TiH_{x=0,0.8}$ compounds at 4.2 and 225 K is shown in Fig. 1. Table 4 summarises the results of saturation magnetisation, anisotropy constants (K_1, K_2) and anisotropy field determination. The saturation magnetisation is obtained by fitting a Weiss and Forrer [11–13] expression from high fields. These measurements confirm that, in $YFe_{11}TiH_x$, the sublattice exhibits uniaxial anisotropy at all temperatures and introducing interstitial hydrogen atoms not only increase the Curie temperature and saturation magnetisation, but also markedly change the magnetocrystalline anisotropy properties. The ^{57}Fe Mössbauer spectra recorded at 4.2 and 290 K for the $YFe_{11}TiH_x$ compounds with $x=0$ and 1.9 were analysed. Examples of spectra at 4.2 K are shown in Fig. 2. The spectra were interpreted by taking account of the preferential occupation of Ti atoms and using a binomial distribution for calculating the probability of possible nearest-neighbour configuration [14,15]. As the spectra are rather complex, only average hyperfine field values were obtained with three different iron sites hf(8j)>hf(8i)>hf(8f), in agreement with the sequence of the magnetic moments determined by neutron diffraction. These values are listed in Table 5.

Table 4
Magnetic characteristics of $YFe_{11}TiH_x$ at 4.2 and 225 K

	$YFe_{11}Ti$	$YFe_{11}TiH_{0.9}$	T(K)
H_A(T)	5.7 (7)	8.0 (6)	4.2
	4.8 (2)	6.2 (2)	300
k_1(J/kg)	361	520	4.2
	325	498	300
k_2(J/kg)	1728	3111	4.2
	1330	2208	300
$M_s(\mu_B/f.u)$	18.3	22.9	4.2
	16.9	20.7	300

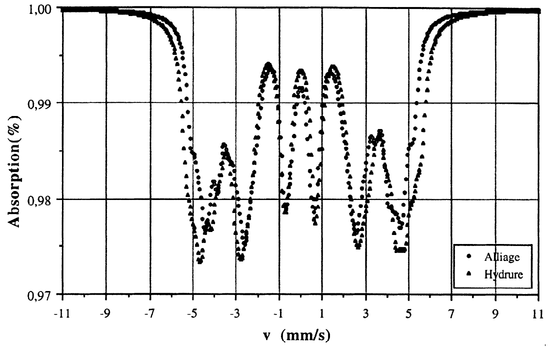

Fig. 2. ^{57}Fe Mössbauer spectra of $YFe_{11}Ti$ (alloy) and $YFe_{11}TiH_{1.9}$ (hydride) at 4.2 K.

4. Conclusion

By neutron diffraction, we have determined in $RFe_{12-x}M_x$ compounds, a second hydrogen attractive site, when the interstitial content is $y>1$. We have shown that insertion of hydrogen atoms modifies the spin reorientation process occurring in $HoFe_{11}Ti$. From magnetisation and Mössbauer spectroscopy measurements, it is seen that the magnetic anisotropy is changed drastically in the in the $YFe_{11}TiH_x$ system. Finally, we observe that most of the magnetic properties are improved upon hydrogenation.

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Table 5
^{57}Fe hyperfine fields of $YFe_{11}TiH_x$ at 4.2, 80 and 290 K

	$YFe_{11}Ti$	$YFe_{11}TiH_{1.9}$	T(K)
Hf(T)-8i	27.7	29.8	4.2
	27.8	29.4	80
	23.9	26.3	290
Hf(T)-8j	31.0	32.9	4.2
	31.0	32.6	80
	26.8	28.7	290
Hf(T)-8f	22.8	25.1	4.2
	24.0	25.6	80
	20.3	20.3	290

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