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Structural and magnetic properties of RFe_2H_5 hydrides (R=Y, Er)

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Abstract

The structural and magnetic properties of RFe_2 hydrides (R=Y, Er) synthesized under high hydrogen pressures of 10 kbar and 373 K, have been investigated. Both saturated RFe_2H_x hydrides absorb about 5 H/f.u. and crystallize in the same type of orthorhombic structure (Imm2 space group), with $a=5.437(1)$ Å, $b=5.850(1)$ Å and $c=8.083(1)$ Å for YFe_2H_5 and $a=5.424(1)$ Å, $b=5.793(1)$ Å and $c=8.009(1)$ Å for $ErFe_2H_5$. The large hydrogen pressure, necessary to reach 5 H/f.u. can be attributed to a partial filling of all types of available interstitial sites. YFe_2H_5 displays a weak ferromagnetic behavior, which is almost independent of the temperature. $ErFe_2H_5$ shows also a weak magnetization at high temperature whereas below 20 K its magnetization sharply increases due to Er magnetic ordering.

Keywords: Hydride; High pressure; X-ray diffraction; Magnetism

1. Introduction

Hydrogen absorption in intermetallic compounds of rare earth and transition metal has raised interest in both fundamental and application field (H storage, batteries . . .). In RFe_2 compounds, hydrogen absorption leads to the formation of several single-phase hydrides, which crystallize in different structures, derived from that of the parent compound [1,2]. Lowering of the crystal symmetry has been related to hydrogen ordering in preferential interstitial sites [2]. In all RFe_2 hydrides the changes of the crystal structure accompanied by an increase of the cell volume, leads to a change of the magnetic properties. The increase of the Fe–Fe distances and the change of the interatomic bonds, due to various H surrounding explain this evolution [3]. Recently, Shashikala et al. [4] have observed that $ErFe_2$ can absorb up to 5 H/f.u. under high pressure, to form a hydride with an orthorhombic structure ($a=7.99$ Å, $b=10.81$ Å, $c=5.78$ Å). However no more information was given about the structural and the magnetic properties of this new hydride. One remaining question is also whether larger amount of hydrogen can be stored in RFe_2 compounds under very high hydrogen pressures.

In this purpose, YFe_2 and $ErFe_2$ hydrides have been submitted to hydrogen pressure of up to 10 kbar. The resulting hydrides were analyzed by X-ray and magnetic measurements. The results will be presented and discussed as a function of H content.

2. Experimental

The YFe_2 and $ErFe_2$ intermetallic compounds were synthesized by induction melting and characterized as in Ref. [2]. The samples were found single-phase and homogeneous with a C15 cubic structure and cell parameters $a=7.36$ Å and 7.28 Å, respectively. Pieces of the intermetallic compounds were placed in the piston-cylinder high pressure apparatus described in [5] and outgased 16 h at 100°C. Then the hydrogen, compressed to 100 MPa, was introduced from a pressure intensifier. Further compression (within the range up to 1.5 GPa) has been performed by using a hydraulic press of 100 t capacity. The temperature of the high pressure apparatus has been kept constant to 100°C by using a conventional temperature control system. After 1–25 days hydrogen exposure, the samples were quenched and kept into liquid nitrogen, until the X-ray and magnetic measurements could be performed. The X-ray diffraction (XRD) patterns were registered with a D8 Brucker diffractometer between 10 and 120° in 2θ and a

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step of 0.02° (Cu K_α wavelength). They were refined with the Rietveld method, using the Fullprof program [6]. The magnetic measurements were performed from 4.2 to 290 K with a DSM8 Manics Magneto-susceptometer for applied fields up to 1.8 T.

3. Results

3.1. Crystal structure determination

The XRD patterns of YFe_2H_x and $ErFe_2H_x$ compounds after hydrogenation at 10 kbar and 473 K, looks like the XRD pattern of $ErFe_2H_{4.8}$ published by Shashikala et al. [4]. After a week, additional reflections corresponding to a rhombohedral phase were observed for both hydrides, indicating the occurrence of hydrogen desorption. The analysis by thermal decomposition of the hydrogen content in both saturated samples, indicated about 5 H/f.u. In the further part of this paper the saturated hydrides will be denoted as YFe_2H_5 and $ErFe_2H_5$. The XRD patterns of YFe_2H_5 and $ErFe_2H_5$ were indexed in a centered orthorhombic cell with $a=5.437(1)$ Å, $b=5.850(1)$ Å and $c=8.083(1)$ Å for YFe_2H_5 and $a=5.424(1)$ Å, $b=5.793(1)$ Å and $c=8.009(1)$ Å for $ErFe_2H_5$. The cell proposed in Ref. [4] could not be used to index the YFe_2H_5 pattern even with larger cell parameters. Compared to the cubic cell of the RFe_2 parent compounds and taking into account the large cell volume increase (29 and 30.6%), the a and b parameters are divided by about $\sqrt{2}$ whereas the c parameter is almost unchanged. The R, Fe and H site positions were derived from that of the $Fd\bar{3}m$ space group with appropriate transformations, and could be described in the space group Imm2 (No. 44) as given in Table 1. The hydride XRD patterns were refined with this new structure and good agreement was obtained as reported for YFe_2H_5 in Table 2 and in Fig. 1. For $ErFe_2H_x$ a small contribution of a second cubic phase (8%) with $a=7.90$ Å, must be added to refine correctly its XRD pattern (Table 3). A hydrogen content of 5 H/f.u. leads to an increase of 2.9 Å^3/H, which is in good agreement with the values obtained for other hydrides. Interatomic distances calculated in these orthorhombic structures are reported in Table 4. The 2 Fe sites display more different surrounding than the two Y or Er atoms. This difference may result from a stronger influence of the interstitial hydrogen on their Fe neighbors.

3.2. Magnetic properties

The magnetization curves of YFe_2H_5 show a ferromagnetic behavior at 6 and 290 K (Fig. 2) with a saturation magnetization $M_S=0.8$ μB/f.u. at 6 K. In Fig. 3, the temperature dependant magnetization of YFe_2H_5 is compared to that of $YFe_2H_{4.2}$ and $YFe_2H_{3.5}$. The magnetization of YFe_2H_5 is significantly reduced compared to that of the hydrides with lower H content and increases only slightly as the temperature decreases. After a week a wide transition is observed between 100 and 150 K, which can

Table 1
Change of the atomic site symmetry and coordinates of Y, Fe and H from the cubic space group $Fd\bar{3}m$ (Non-centrosymmetric setting) to the orthorhombic space group Imm2

S.G.	$Fd\bar{3}m$ No. 227				Imm2 No. 44			
	Site	*x*	*y*	*z*	Site	*x*	*y*	*z*
R	8a	0	0	0	2a	0	0	0
					2b	0	1/2	3/4
Fe	16d	5/8	5/8	5/8	4c	1/4	0	5/8
					4d	0	1/4	3/8
D (A2B2)	96g	7/16	7/16	1/4	4c	1/8	0	1/4
					4c	3/8	0	0
					4d	0	1/8	3/4
					4d	0	3/8	0
					8e	3/16	5/16	15/16
					8e	5/16	5/16	5/16
					8e	3/16	5/16	9/16
					8e	3/16	3/16	3/16
D (AB3)	32e	13/32	13/32	13/32	4c	3/16	0	13/32
					4c	5/16	0	27/32
					4d	0	3/16	19/32
					4d	0	5/16	5/32
D (B4)	8b	1/2	1/2	1/2	2a	0	0	1/2
					2b	0	1/2	1/4

Table 2
Refined parameters and atomic positions in the space group Imm2 for YFe_2H_5

S.G. Imm2				
Cell parameters	$a = 5.437(1)$ Å	$b = 5.850(1)$ Å	$c = 8.083$ (1) Å	V=257 $Å^3$
Atom	x	y	z	B ($Å^2$)
Y1	0	0	−0.020(1)	0.63
Y2	0	0.5	0.746(1)	0.63
Fe1	0.239(1)	0	0.616(1)	0.36
Fe2	0	0.260(1)	0.369(1)	0.36
Rp: 12.7%	R_F: 8.2%			

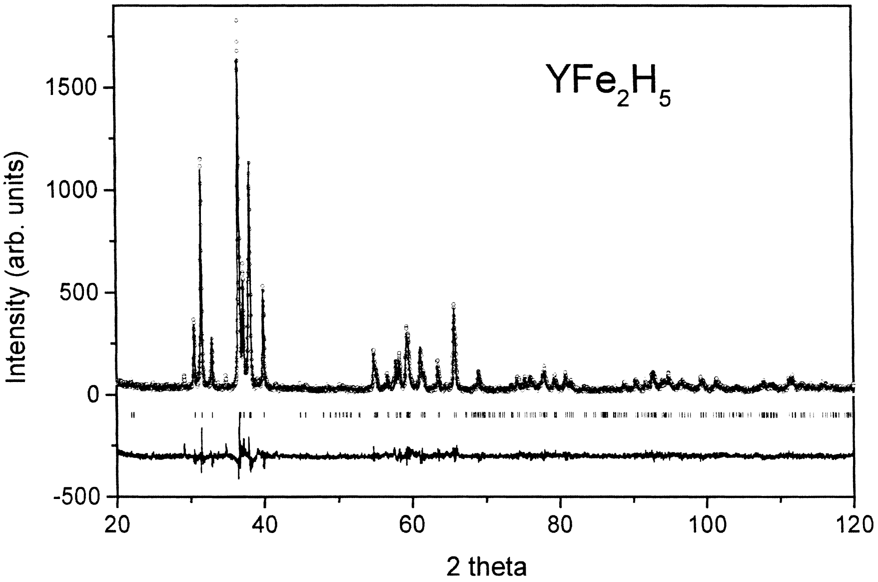

Fig. 1. Refined XRD pattern of YFe_2H_5, with the values of Table 2. (○) Experimental curve, (—) calculated curve, difference curve (bottom), (|) hkl line positions ($\lambda = 1.54178$ Å). The pattern was measured with a D8 Brucker diffractometer.

be related to a small amount of $YFe_2H_{4.2}$ due to H desorption as observed in the XRD patterns. The magnetization curves versus field of $ErFe_2H_5$, reported in Fig. 4 are not saturated. The superposed susceptibility is maximum at 10 K (1.5 10^{-1} μB/kOe) and decreases continuously down to 1.7 10^{-3} μB/kOe at 290 K. The temperature dependent magnetization M(T) of $ErFe_2H_5$, measured with different applied magnetic fields, and the M_S magnetization extrapolated at H=0 from the M(H) curves are reported on Fig. 5. The values of M_S scale with M(T) measured at 0.2 T. The sharp increase of M(T) observed below 30 K, should be attributed to erbium

Table 3
Refined parameters and atomic positions for the orthorhombic and cubic phases in $ErFe_2H_5$ hydride

Orthorhombic phase		S.G. Imm2		
Cell parameters	$a = 5.424(1)$ Å	$b = 5.793(1)$ Å	$c = 8.009(1)$ Å	V=252 $Å^3$
Atom	x	y	z	B ($Å^2$)
Er1	0	0	−0.012(1)	1.3
Er2	0	0.5	0.753(1)	1.3
Fe1	0.241(1)	0	0.628(1)	0.2
Fe2	0	0.235(1)	0.368(1)	0.2
R_F: 7.7%				
Cubic phase				
Cell parameter	$a = 7.900$ Å			V=493 Å
Atom	x	y	z	B ($Å^2$)
Er	0.125	0.125	0.125	1.4
Fe	0.5	0.5	0.5	2.8
$R_F = 8\%$				
Rp: 9.6%				

Table 4
Number of neighbors N and averaged interatomic distances between R and Fe nearest neighbors in RFe_2H_5 hydrides. The values in bracket correspond to the maximum distance deviation from the average value

Central atom	Neighbor atom	N	d (Å) R=Y	d (Å) R=Er
Fe1	Fe	6	2.80 (0.08)	2.78 (0.17)
Fe1	R	6	3.35 (0.13)	3.33 (0.16)
Fe2	Fe	6	2.87 (0.17)	2.85 (0.22)
Fe2	R	6	3.30 (0.20)	3.27 (0.17)
R1	Fe	12	3.32 (0.18)	3.31 (0.14)
R1	R	4	3.48 (0.01)	3.45 (0.01)
R2	Fe	12	3.33 (0.06)	3.29 (0.15)
R2	R	4	3.48 (0.01)	3.45 (0.01)

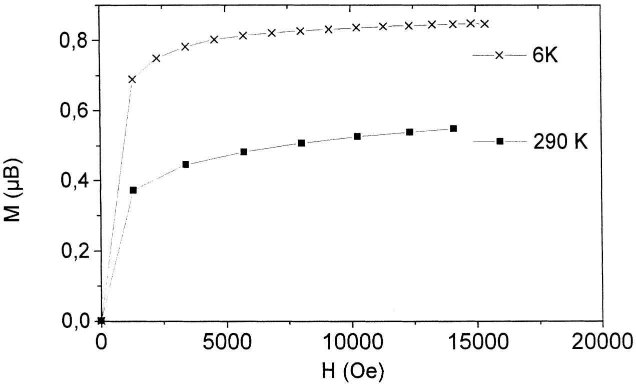

Fig. 2. Magnetization versus field of YFe_2H_5 at 6 and 290 K.

magnetic ordering, since as observed for YFe_2H_5 the Fe magnetization should remain almost constant at low temperature. The minimum at 20 K, observed in M(T) at 0.2 T and $M_S(T)$, can be related to a compensation temperature $T_{comp.}$ between the Er and Fe sublattice.

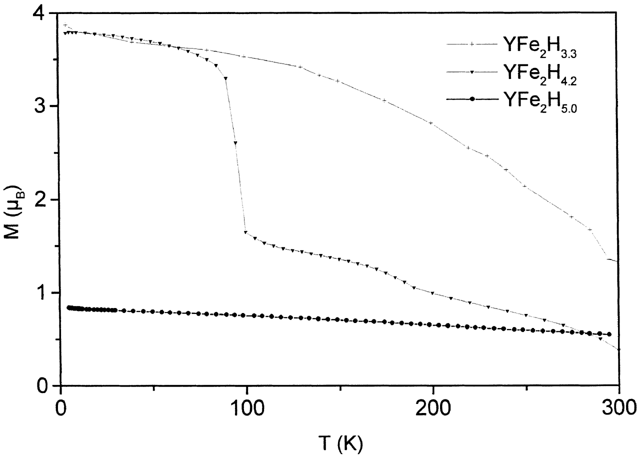

Fig. 3. Temperature dependant magnetization of YFe_2H_x compounds for $x = 3.3$, 4.2 and 5 H/f.u.

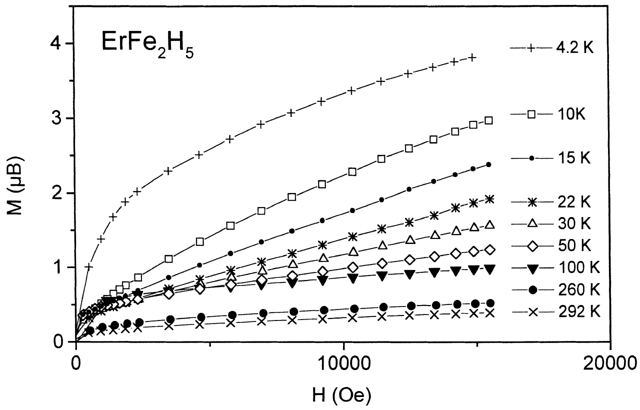

Fig. 4. Magnetization versus field of YFe_2H_5 between 4.2 and 290 K.

4. Discussion

Hydrogen absorption under high pressure leads to similar orthorhombic phases for both YFe_2H_5 and $ErFe_2H_5$. The structural distortions of the RFe_2 cubic cell, upon hydrogen absorption have been attributed to various filling of hydrogen in non-equivalent interstitial sites. In the cubic Fd 3 m space group three different interstitial sites are available: A2B2 (96g), AB3 (32e) and B4 (8b) (A=R and B=Fe). According to both geometrical and thermodynamical criteria the 96g sites (A2B2) sites are preferentially occupied for low H content. The rhombohedral distortion in $ErFe_2H_{3.5}$ (R 3 m space group) was attributed to the filling of AB_3 sites [1] whereas in $YFe_2H_{3.5}$ only A2B2 sites were found occupied [7]. In the orthorhombic Imm2 space group the 96g position splits into eight positions, the 32e into four positions and the 8b into two positions (Table 1). Due to the 30% cell volume increase, all these sites have a radius larger than 0.4 Å. A statistical calculation taking into account the minimal

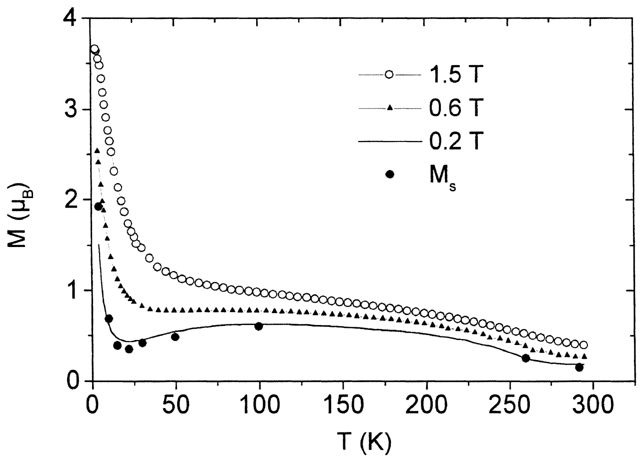

Fig. 5. Temperature dependant magnetization at different applied fields and saturation magnetization M_s in $ErFe_2H_5$.

distance between two hydrogen atoms $R_{H-H} \approx 2.1$ Å, shows that the hydrogen content of 5 H/f.u can be reached only if the three types of A2B2, AB3 and B4 sites are partially occupied. With only A2B2 sites we reach about 3 H/f.u. and with A2B2 and AB3 sites 4 H/f.u. as maximal H content. Since the B4 sites are thermodynamically less stable than the A2B2 and AB3 sites, a very high hydrogen pressure is therefore required to fill these new sites.

Bulk magnetization of YFe_2H_5 and $ErFe_2H_5$ are strongly reduced compared to the hydrides with lower H content. In YFe_2H_x hydrides, the magnetization is dominated by the Fe–Fe interaction and M_{Fe} is reduced from 1.95 μB for $x=3.6$ to 0.4 μ_B for $x=5$. This decrease of the bulk magnetization can result either from a reduction of the Fe moment or to a non-collinear orientation of the Fe moments as proposed by Shashikala et al. [8]. Since in the orthorhombic structure, there are two different Fe sites with different surrounding, two different orientations of the Fe moments cannot be excluded. In $YFe_2D_{4.2}$ the metamagnetic transition observed at 90 K [3] can result from a change of Fe moment orientation under an external field. In $ErFe_2H_5$, the small value of the compensation temperature $T_{comp.}$ (20 K) observed for $ErFe_2H_5$ agrees well with the reduction of $T_{comp.}$ versus H content observed in $ErFe_2H_x$ compounds by Fruchart et al. [1]. This decrease reflects the lowering of the exchange interaction between rare earth and transition metal as the interatomic distances increase. A fanning of the Er moment has been observed by Fish et al. [9] in $ErFe_2H_{3.5}$ assuming an antiparallell collinear coupling of the Er and Fe moments as in $ErFe_2$. However since there are two different Er sites in orthorhombic $ErFe_2H_5$, a non-collinear orientation of the Er moments can be expected. The large value of the superposed susceptibility in the M(H) curves may support this assumption. Further experiments, like ^{57}Fe Mössbauer spectroscopy and neutron diffraction experiments will be performed to check the origin of the strong reduction of the bulk magnetization observed in both YFe_2H_5 and $ErFe_2H_5$ hydrides, compared to the hydrides with lower H content.

5. Conclusion

The synthesis of RFe_2 hydrides (R=Y, Er) under 10 kbar hydrogen, leads to the formation of orthorhombic RFe_2H_5 hydrides. Their crystal structures were refined in the space group Imm2 with two different R and Fe sites. The analysis of the possible interstitial hydrogen sites shows that according to geometrical criterion all type of A2B2, AB3 and B4 interstitial sites should be occupied to reach the concentration 5 H/f.u. The reduction of the bulk magnetization observed for both compounds compared to hydrides with lower H content, may result either from a fanning of the Fe and Er moments, or from a non-collinear orientation of the magnetic moments. In addition the decrease of the compensation temperature for $ErFe_2H_5$ indicates a lowering of the exchange interaction between Er and Fe moments.

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