

HYDROGEN INSERTION IN HARD MAGNETIC MATERIALS BASED ON RARE-EARTH AND IRON : THE EXAMPLE OF THE R_2Fe_{17} PHASES¹

Olivier Isnard

Laboratoire de Cristallographie du CNRS, associé à l'Université J. Fourier, BP 166X, 38042 Grenoble cédex France and the Institut Universitaire de France, Maison des Universités, 103 boulevard Saint Michel, F-75005 Paris, France, also at Institut Laue Langevin, rue Jules Horowitz ,BP 156X, 38042 GRENOBLE cédex 9 France

Abstract

The insertion of hydrogen atoms within the crystal structure of R_2Fe_{17} type inter-metallic compounds has been found to dramatically influence the physical properties of these phases. The crystal structure of these compounds has been investigated by both X-ray and neutron diffraction. The localisation of the hydrogen within the crystal lattice is described. Two different interstitial sites are filled depending upon the hydrogen content. The maximum hydrogen content that can be inserted reversibly in the R_2Fe_{17} crystal structure is found to be 5 atoms per formula unit for the light rare earth values which decreases down to 3 atoms per formula unit for the heaviest rare-earth elements. In situ neutron diffraction investigation has been undertaken in order to determine the relative stability of the octahedral versus tetrahedral sites. At low temperature the dynamic of the hydrogen atoms has been evidenced by ^{57}Fe Mössbauer spectroscopy and more recently analyzed in the light of neutron quasielastic neutron scattering. The emphasis is given on the description of the hydrogen effect on the magnetic properties of these compounds. The magnetic properties are probed by magnetization measurements up to 24T, Mössbauer spectroscopy, X-ray absorption spectroscopy, and neutron scattering. It will be seen that even if hydrogen is a non magnetic element, it influences almost all the magnetic properties of these compounds : magnetisation, ordering temperature, magnetocrystalline anisotropy, exchange interactions...

Keywords: hard magnetic materials, Hydrogen, intermetallic compounds.

1. Introduction

The R_2Fe_{17} compounds (R= rare earth metal) are among the richest of all binary rare-earth iron intermetallics. Depending on the rare earth size, they are known to crystallize with the rhombohedral (R-3m) Th_2Zn_{17} structure type for light R elements or hexagonal ($P6_3/mmc$) Th_2Ni_{17} structure type for the heaviest R elements. The negative R-Fe exchange interaction leads to a parallel coupling between R and Fe magnetic moments (ferromagnetic order) for the light rare-earth and a ferrimagnetic coupling for the heaviest rare-earth.

¹ Invited lecture presented to TIM-05 conference, 24-25 November, 2005, Timisoara

Unfortunately, R_2Fe_{17} compounds have a too low Curie temperature for permanent magnet applications, and rather moderate magnetocrystalline anisotropy, thus hampering applications as permanent magnet. Insertion of light elements such as H, C or N in the R_2Fe_{17} series has been found to modify a large part of the magnetic properties of these compounds thus becoming prospective candidates for metal-bonded permanent magnets. The most spectacular changes are increase of the Curie temperature T_C and of the magnetization M_S upon interstitial insertion [1-4]. Hydrogenated R_2Fe_{17} compounds are suitable materials for fundamental studies because a solid solution behaviour of hydrogen insertion is observed [1,5]. This allows modulation of stoichiometry upon reaction and a consequent controlled variation of the magnetic properties. This review we will present the main results obtained in this field among the last years and describe the state of understanding and give useful references.

2. Experimental

The R_2Fe_{17} compounds have been synthesized in a water-cooled copper crucible by melting 99.95% pure R and 99.99% pure iron in a high frequency induction furnace under argon atmosphere. Sample homogeneity was optimized by wrapping small pieces of the induction melted ingot in tantalum foil, sealing them in evacuated silica tubes, and annealing them at 1270 K for at least two weeks. Hydrogen insertion was then performed at 300 K in a dedicated stainless steel autoclave under a deuterium pressure of about 5MPa leading to a stable hydride. A 10-minute thermal activation at 580 K has been used to initiate the reaction. The deuterium uptake was determined by gravimetric methods, and the accuracy of the interstitial concentration can be estimated to about 2%. The estimated hydrogen content has been confirmed by neutron diffraction [6-8]. The purity of the samples has been confirmed by powder x-ray diffraction. The samples were found to be single phase with traces of α -iron. High accuracy lattice parameters have been obtained with a Guinier-type focusing camera and iron K_{α_1} radiation.

The magnetic ordering temperature, T_C , of $R_2Fe_{17}H_x$ compounds has been obtained on a Faraday torque balance with 5 K per minute heating or cooling. A sample of ca. 50 mg was sealed under vacuum in a small silica tube in order to prevent oxidation of the sample during heating. The saturation magnetization has been obtained at 5 and 300 K by the extraction method in continuous fields ranging up to 7 T. The high field magnetisation measurements have been performed as described in reference [9].

3. Results and Discussions

According to x-ray and neutron diffraction investigations [4,7,8] the structure of the $R_2\text{Fe}_{17}$ hydrides is closely related to the structure of the starting $R_2\text{Fe}_{17}$ compounds. Previous studies have determined the hydrogen location: two different interstitial sites have been observed in the R environment both in the rhombohedral and hexagonal structures. The first one is which is a distorted octahedron, the second one is a tetrahedron and appears to be less occupied. These two hydrogen sites, respectively referred to as D1 and D2 are shown in figure 1 in the case of the rhombohedral structure retained by the light rare-earth elements.

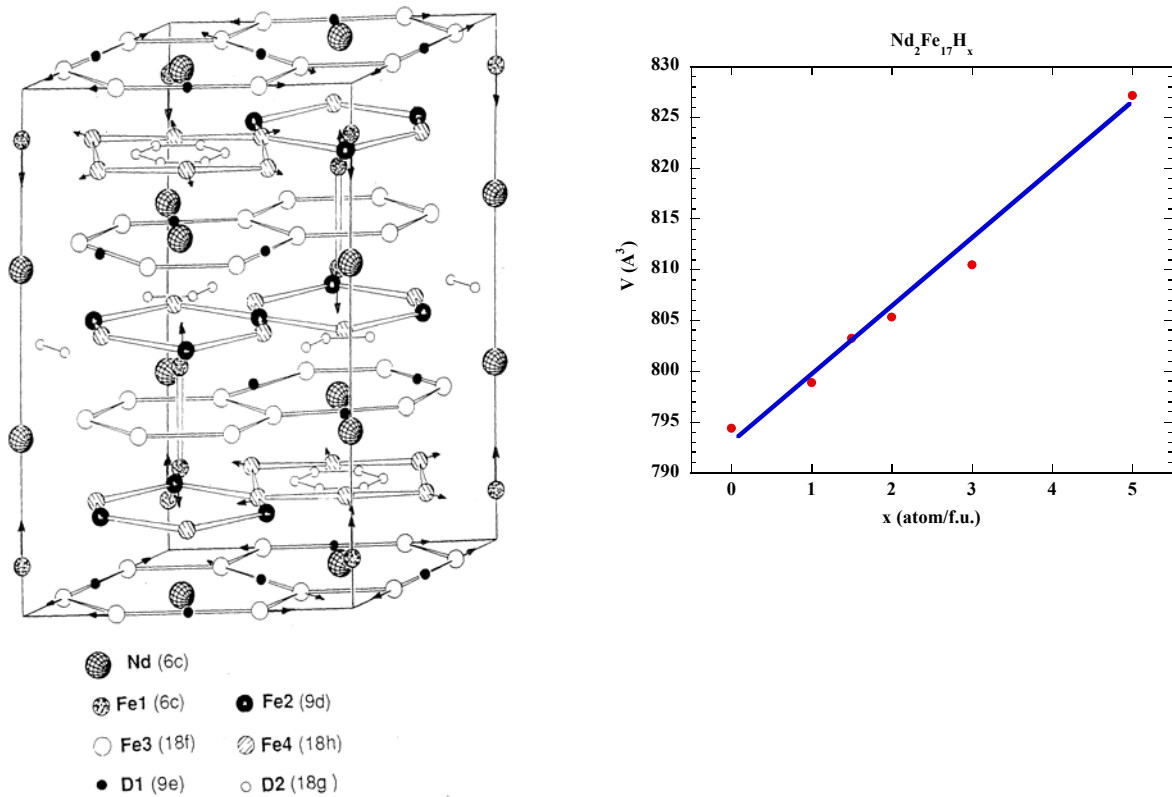


Figure 1. Left : Crystal structure of the $\text{Nd}_2\text{Fe}_{17}\text{H}_x$ compounds. Right: Hydrogen composition dependence of the unit cell volume in the $\text{Nd}_2\text{Fe}_{17}\text{H}_x$ compounds.

The insertion of hydrogen induces a significant unit cell increase as shown in figure 1-b. The mean expansion rate is about 2.3 \AA^3 per hydrogen atom inserted in the $R_2\text{Fe}_{17}$ compounds [8-11]. It is worth to note that this cell expansion is fairly anisotropic it occurs rather along the basal plane than along the c -axis of the hexagonal lattice. The unit cell expansion is smaller for the heavy rare earth containing $R_2\text{Fe}_{17}$ than with light rare earths, indeed the latest

compounds can uptake larger hydrogen amount. The maximum hydrogen content that can be accommodated in these R_2Fe_{17} compounds decreases when the rare-earth size and consequently the unit cell volume decreases. Whereas up to 5 H atoms per formula unit can be inserted for the light rare-earth elements only 3 H atoms can be up taken for the heaviest R containing compounds-see figure 2-. Neutron diffraction experiments have shown that this effect can be explained by a different filling of the tetrahedral site which is less occupied for the heaviest R [6]. A filling scheme of these interstitial sites by H atoms has been proposed and confirmed by in situ neutron diffraction investigation [6]. The octahedral interstitial site has been found to be much more stable in temperature than the small tetrahedral one. Due to electrostatic repulsion between neighbouring H atoms, at most two out of the six possible D2 interstitial sites can be occupied simultaneously. This explains the maximum hydrogen content of 5 H atoms per formula unit : 3 on the octahedral sites and depending on the rare-earth size and two H per formula unit on the tetrahedral one[13, 15].

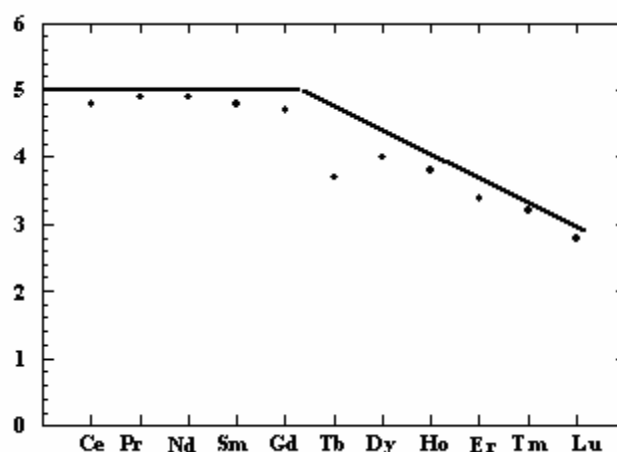


Figure 2. Evolution of the maximum hydrogen content that can be inserted in the $R_2Fe_{17}H_x$ compounds versus the R nature.

As can be seen in figure 3, there is a substantial increase in the ordering temperature upon hydrogen insertion into the R_2Fe_{17} phases, an increase which results from the negative pressure effect of the interstitial element on the lattice. Indeed the R_2Fe_{17} phases are characterized by an ordering temperature that decreases significantly upon application of an external pressure [14].

As can be seen from figure 4 there is a continuous increase of T_C versus H content but a slight saturation appears for the largest H concentration. Fundamentally, hydrogen insertion has two effects: lattice expansion and contribution to the chemical bonding. It has been shown that the main cause of the Curie temperature increase is the lattice expansion [15]. This results

from the peculiar structure of the R_2Fe_{17} phases which have very short inter-atomic Fe-Fe distances, distances that can lead to local negative exchange interactions. The hydrogen induced unit cell expansion thus promotes longer Fe-Fe instances which according to the Salter Néel curves leads to stronger Fe-Fe exchange interactions. The effect of hydrogen in the $R_2Fe_{17}H_x$ can be compared to an internal pressure effect on the lattice of about -40kBar for $x=5$. It is worth to note that this effect is reversible since applying an external pressure on the hydrides leads to a reduction of the ordering temperature [16,17].

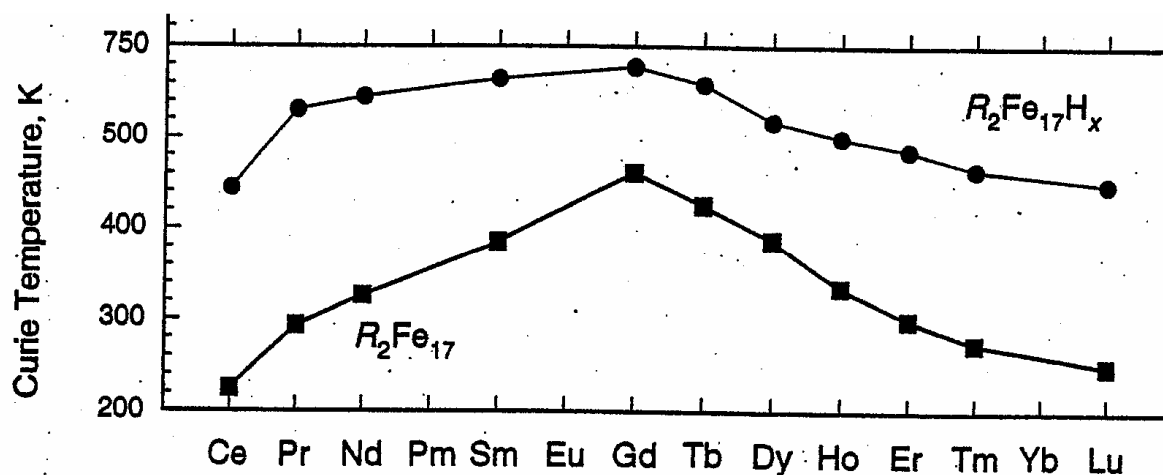


Figure 3. Ordering temperature of the $R_2Fe_{17}H_x$ compounds.

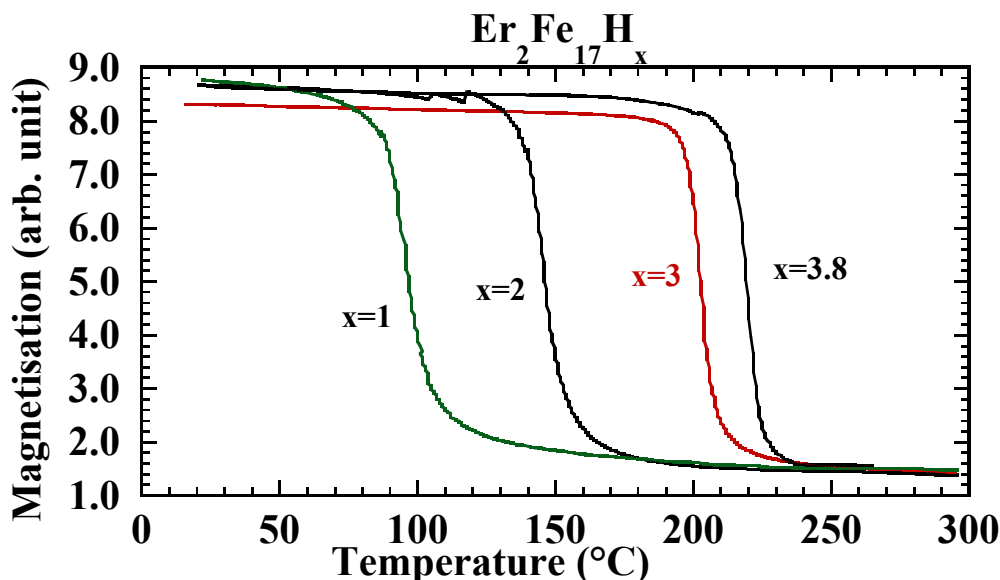


Figure 4. Thermomagnetic curves recorded for the $Er_2Fe_{17}H_x$ compounds.

In spite that hydrogen is a non magnetic element, many other magnetic properties are modified upon H insertion. Even the type of ordering which is helimagnetic for R=Ce or Lu becomes ferromagnetic after H insertion [4,8,18,19]. Such spectacular effect is well illustrated is figure 5 by a comparison of the magnetization curves of Ce₂Fe₁₇ and Ce₂Fe₁₇H₅. This change of magnetic order is understood as resulting from the large enhancement of the Fe-Fe exchange interaction. The case of the Ce compounds has been extensively studied since these compounds also exhibits by far the largest cell expansion upon H insertion and a change of Ce valence state to a trivalent state was expected [8,19]. A detailed investigation has been carried out using X-ray absorption spectroscopy from synchrotron radiation [8], but only a small evolution of the valence state of Ce has been observed upon hydrogenation. This result confirms that the changes of magnetic type of the Ce₂Fe₁₇H_x the properties can be attributed to the iron sublattice only [19].

Table 1. Saturation magnetization M_s , ordering temperature T_C (K) and hydrogen content of the investigated $R_2Fe_{17}H_x$ compounds.

Compound	M_s ($\mu_B/u.f.$)		T_C (K)	ΔT_C (K)	x (H/f.u.)
	5K	300K			
Ce ₂ Fe ₁₇	29.7	-	225 (T _N)		-
Ce ₂ Fe ₁₇ H _x	34.7	27.2	444	"229"	4.8
Pr ₂ Fe ₁₇	36.4	-	293		-
Pr ₂ Fe ₁₇ H _x	41	35.6	531	238	4.9
Nd ₂ Fe ₁₇	38	26.2	326		-
Nd ₂ Fe ₁₇ H _x	40,2	35,6	545	219	4.9
Sm ₂ Fe ₁₇	35.4	27.5	385		-
Sm ₂ Fe ₁₇ H _x	38.4	35.6	565	180	4.7
Gd ₂ Fe ₁₇	21.5	17.6	461		-
Gd ₂ Fe ₁₇ H _x	22.2	21.7	578	117	4.4
Tb ₂ Fe ₁₇	20.0	17.6	425		-
Tb ₂ Fe ₁₇ H _x	19.0	20.1	559	134	3.6
Dy ₂ Fe ₁₇	16.2	14.6	387		-
Dy ₂ Fe ₁₇ H _x	16.7	20.1	518	131	4
Ho ₂ Fe ₁₇	19.5	18.0	335		-
Ho ₂ Fe ₁₇ H _x	19.7	24.6	500	165	3.8
Er ₂ Fe ₁₇	17.9	12.5	300		-
Er ₂ Fe ₁₇ H _x	17.7	23.6	486	186	3.4
Tm ₂ Fe ₁₇	21.2	-	274		-
Tm ₂ Fe ₁₇ H _x	24.7	27.5	465	191	3.2
Lu ₂ Fe ₁₇	34.2	-	270 (T _N)		-
Lu ₂ Fe ₁₇ H _x	32.2	26	449	"179"	2.8
Y ₂ Fe ₁₇	34.2	19.9	327		-
Y ₂ Fe ₁₇ H _x	34.6	29.5	509	182	3.5
Th ₂ Fe ₁₇	30.5	14.2	315		-
Th ₂ Fe ₁₇ H _x	35.2	31	471	156	5

The saturation magnetization is also modified: as can be seen from Table 1, even the low temperature saturation magnetizations of the ferromagnetic compounds are increased of magnetisation after hydrogenation. According to neutron diffraction investigations or Mössbauer spectroscopy, this increase involves all iron sites. This was connected to the narrowing of the 3d band, a narrowing resulting from the lattice expansion upon H insertion within the $R_2\text{Fe}_{17}$ lattice.

For other $R_2\text{Fe}_{17}$ phases, the magnetic phase diagram is changed after H insertion this has been found to be the case at least for $\text{Tm}_2\text{Fe}_{17}\text{H}_x$ and $\text{Pr}_2\text{Fe}_{17}\text{H}_x$ compounds [18,20]. For example, a spin reorientation is observed at 90K in $\text{Tm}_2\text{Fe}_{17}$ in the temperature dependence of both the a.c. susceptibility and the Mössbauer spectra. Above and below 90K, the iron magnetic moments are aligned within the basal plane and along the c-axis respectively.

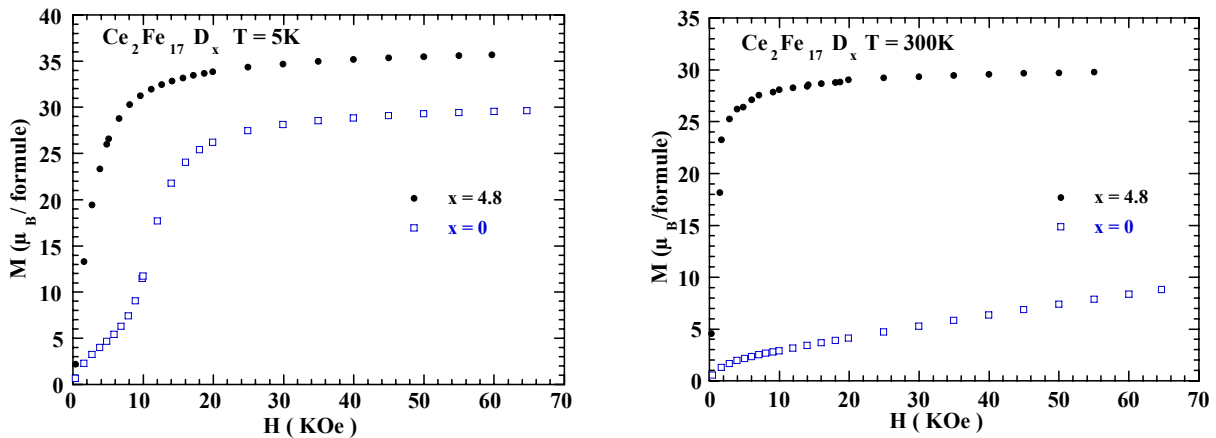


Figure 5. Comparison of the isothermal magnetization curves recorded for $\text{Ce}_2\text{Fe}_{17}$ and $\text{Ce}_2\text{Fe}_{17}\text{H}_{4.8}$ compounds[4].

The spin reorientation in $\text{Tm}_2\text{Fe}_{17}$ results from a competition between the thulium and iron magnetic anisotropies. The Tm and Fe sublattices anisotropies prefer an alignment of the magnetization along and perpendicular to the c-axis respectively. Below 90 K the thulium anisotropy dominates and favours an axial alignment of the spins. It has been revealed by both the a.c. susceptibility measurements and the Mössbauer spectra [20], that hydrogen insertion into $\text{Tm}_2\text{Fe}_{17}$ suppresses this spin reorientation, and that in $\text{Tm}_2\text{Fe}_{17}\text{H}_{3.2}$ the iron magnetic moments are oriented within the basal plane of the unit cell from 4.2 to 295K. This change can not be attributed to the iron sublattice anisotropy since it has been shown [22] that hydrogen insertion has almost no effects on the Fe sublattice contribution to the anisotropy see figure 6 and table 2 [11,22]. Then, the suppression of the spin reorientation is due to a modification of the rare-earth sublattice magnetocrystalline anisotropy. Such reduction of the

R contribution to the magnetocrystalline anisotropy is consistent with high field magnetisation measurements on other $R_2Fe_{17}H_x$ compounds ($R=Sm, Nd...$)[9,23]. Using ^{155}Gd Mossbauer spectroscopy, the modification of the R sublattice magnetocrystalline anisotropy has been connected to the reduction of the crystal electric field gradient V_{zz} experienced at the R nucleus [24]. The corresponding values are summarised in table 2 for the $Gd_2Fe_{17}H_x$ compounds. Here it is not only the cell expansion that modifies the V_{zz} value but mainly the chemical effect of H which becomes the closest neighbour of the rare-earth thus modifying its local environment.

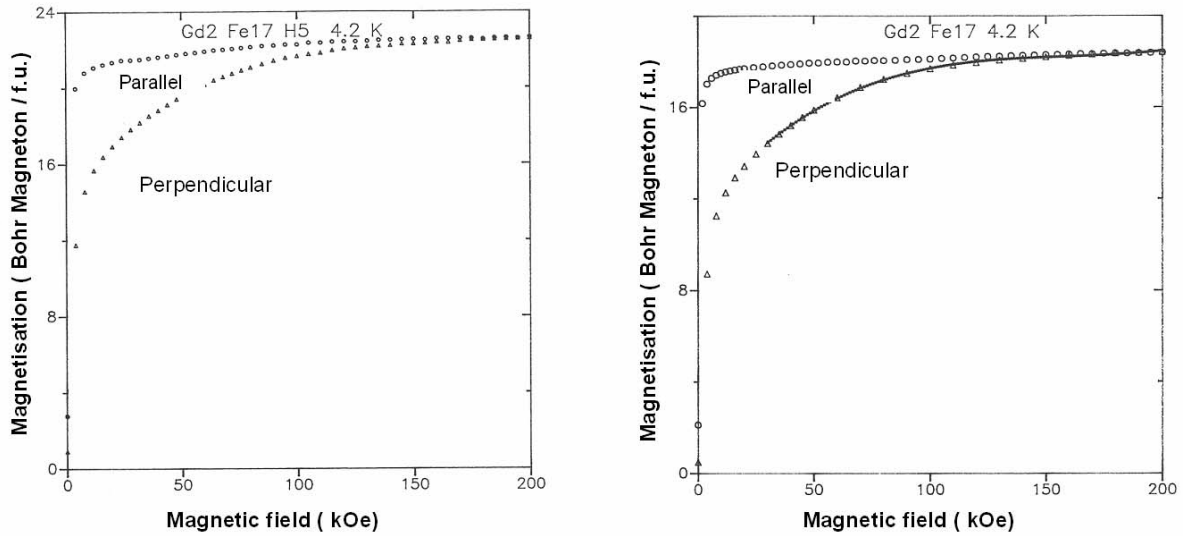


Figure 6. Isothermal magnetization curves recorded when applying the field parallel and perpendicular to the easy magnetization direction of $Gd_2Fe_{17}H_x$ compounds [22].

In the $Pr_2Fe_{17}H_x$ system, hydrogen insertion has been found to induce a spin reorientation of the magnetisation for $x \geq 3$. Mössbauer spectroscopy analysis has shown that at low temperature $Pr_2Fe_{17}H_x$ compounds have uniaxial anisotropy for $3 \leq x < 5$. Unfortunately, above room temperature, none of these phases are exhibiting the axial anisotropy required for permanent magnet applications [18].

Table 2. Crystal electric field gradient [24], Gd-Fe exchange field [25] first order anisotropy [22] parameter of the $Gd_2Fe_{17}H_x$ compounds.

	V_{zz} [24] ($10^{21}V/m^2$)	A_2^0 (Ka_0^{-2})[24]	K_{1Fe} 4,2K (MJ/m^3) [22]	K_{1Fe} 300K (MJ/m^3) [22]	B_{ex} (T) [25]
Gd_2Fe_{17}	4.02 (13)	-351	-2.0(0,3)	-1.5(0,1)	285
$Gd_2Fe_{17}H_3$	2.66 (11)	-233	-2.0(0,3)	-1.1(0,1)	268
$Gd_2Fe_{17}H_5$	~ 0	~ 0	-2.0(0,3)	-0.9(0,2)	247

The rare-earth iron exchange interactions are also very sensitive to the presence of hydrogen. Unlike most of the other magnetic properties that are improved upon H insertion, a significant reduction of the Gd-Fe exchange field has been obtained by high energy inelastic neutron scattering [25], a reduction that has been attributed to the lattice expansion [25,26]. The Gd-Fe exchange field values (B_{ex}) are given in table 2 for the $Gd_2Fe_{17}H_x$ compounds.

Another surprising feature has been reported in the $R_2Fe_{17}H_x$ compounds : hydrogen dynamic has been observed on the tetrahedral D2 site. This hypothesis of H dynamics has been first proposed from Mössbauer spectroscopy analysis [18] and has been recently confirmed by neutron scattering technique [27]. At low temperature the dynamic of hydrogen atoms among the tetrahedral sites is frozen, whereas correlated hopping of two hydrogen atoms is observed at higher temperature.

4. Conclusions

It has been shown that even if hydrogen is a non magnetic element, it influences almost all the magnetic properties of these compounds: magnetisation, ordering temperature, magnetocrystalline anisotropy, exchange interactions. Hydrogen insertion has two main effects on the R_2Fe_{17} compounds : a negative like pressure effect expanding the lattice and a contribution to the chemical bonding. The hydrogen induced modifications of the physical properties originates either from one or both of these effects. Whereas the magnetisation increase and the Curie temperature increase are mainly due to the unit cell expansion, the changes of the magnetocrystalline anisotropy are due to the chemical effect of hydrogen which modifies the the local environment around the rare-earth. Other properties such as the modification of the Ce valence state upon H insertion are induced by both steric and chemical effect of hydrogen.

References

- [1] B. Rupp, G. Wiesinger, J. Magn. Magn. Mater. 71, (1998) 269.
- [2] W. Xiang Zhong, K. Donnelly, J.M.D. Coey, B. Chevalier, J. Etourneau, T. Berlureau, J. Mater. Sci. 23 (1988) 329.
- [3] J.M.D. Coey, H. Sun, J. Man. Magn. Mater. 87 (1990) L251.; K.H.J. Buschow, Rep. Prog. Phys. 54 (1991) 1123.
- [4] O. Isnard, S. Miraglia, D. Fruchart, J. Deportes, J. Magn. Magn. Mater., 103 (1992) 23.
- [5] O. Isnard, S. Miraglia, D. Fruchart, E. Akiba, K. Nomura, J. Alloys&Comp.257(1997)150

- [6] O. Isnard, S. Miraglia, J.L. Soubeyroux, D. Fruchart, A. Stergiou, *J. Less-Common Met.* , 162 (1990) 273.
- [7] O. Isnard, S. Miraglia, J.L. Soubeyroux, D. Fruchart, *Solid State Comm.* 87 (1992) 13.
- [8] O. Isnard, S. Miraglia, D. Fruchart, C. Georgetti, S. Pizzini, E. Dartyge, J.P. Kappler, G. Krill, *Phys. Rev. B*, 49, 15692-15701 (1994).
- [9] O. Isnard, M. Guillot *J. Appl. Phys.*, 98, 033912 (2005).
- [10] F. Grandjean, O. Isnard, D. Hautot, G.J. Long, *Phys. Rev. B*, 63 (2001) 014406.
- [11] I.S. Tereshina, S. Nikitin, K. Skokov, T. Palewski, V. Zubenko, I. Telegina, V.N. Verbetsky, A.A. Salamova, *J. Alloys and Compds* 350 (2003) 264. I.S. Tereshina, S. Nikitin, J. Stepien-Damm, W. Suski, A.A. Salamova, V.N. Verbetsky, *J. Magn. Magn. Mater.* 258 (2003) 427.
- [12] O. Isnard, J.L. Soubeyroux, S. Miraglia, D. Fruchart, L.M. Garcia, J. Bartolome, *Physica* 180-181B (1992) 629.
- [13] O. Isnard, S. Miraglia, J.L. Soubeyroux, D. Fruchart, P. L'Heritier, *J. Magn. Magn. Mater.* 137 (1994) 151.
- [14] M. Brouha, K.H.J. Buschow and A.R. Miedema, *IEEE Trans. Mag.* MAG-10 (1974) 183.
- [15] O. Isnard, S. Miraglia, D. Fruchart, *J. Magn. Magn. Mater.* 140-144 (1995) 981.
- [16] O. Isnard, D. Fruchart, *J. Alloys and Comp.* 205 (1994) 1.
- [17] O. Isnard, R. Zach, S. Niziol, S. Miraglia, D. Fruchart, *J. Magn. Magn. Mater.* 140-144 (1995) 1073.
- [18] D. Hautot, G.J. Long, F. Grandjean, O. Isnard, *J. Appl. Phys.* 86 (1999) 2200.
- [19] D. Hautot, G.J. Long, F. Grandjean, O. Isnard, *Phys. Rev. B* 62 (2000) 11731.
- [20] F. Grandjean, O. Isnard, G.J. Long, *Phys. Rev. B* 65 (2002) 064429.
- [21] G.J. Long, O. Isnard, F. Grandjean, *J. Appl. Phys.*, 91 (2002) 1423.
- [22] O. Isnard, S. Miraglia, D. Fruchart, M. Guillot, *I.E.E.E. trans. on Magn.* 30-6 (1994) 4969.
- [23] O. Isnard, S. Miraglia, M. Guillot, D. Fruchart, *J. Applied Physics.* 75 (1994) 5988.
- [24] O. Isnard, P. Vulliet, A. Blaise, J.P. Sanchez, S. Miraglia, D. Fruchart, *J. Magn. Magn. Mater.* 131(1994) 83.
- [25] O. Isnard, A. Sippel, M. Loewenhaupt, R. Bewley, *J. Phys. Cond. Matter*, 13 (2001)
- [26] N.M. Hong, *Physica B* 226 (1996) 391.
- [27] E. Mamontov, T.J. Udovic, O. Isnard, J.J. Rush, *Phys. Rev. B*, 70 (2004) 214305.