Structural and magnetic phase diagram of YMN₂₋ₓFeₓ(H,D)ₓ compounds (5 ≤ y ≤ 6) synthesized under high H or D gaseous pressure

V. Paul-Boncour a,*, S.M. Filipek b, K. Provost a, F. Couturais a, A. Morawski b

a Université de Paris Est, ICMPE, CNRS-UPEC, UMR7182, 2-8 rue Henri Dunant, 94320, Thiais, France
b Institute of High Pressure Physics, PAS, ul. Sokolowska 29, 01-142, Warsaw, Poland

A R T I C L E   I N F O

Article history:
Received 1 April 2016
Received in revised form 24 August 2016
Accepted 25 August 2016
Available online 27 August 2016

Keywords:
Metal hydrides
Phase diagrams
High gaseous pressure
Neutron diffraction
Magnetic measurements

A B S T R A C T

YMn₂₋ₓFeₓH(D)ₓ compounds with high hydrogen or deuterium content (5 ≤ y ≤ 6) were synthesized under high H or D gaseous pressure (P = 0.8 GPa) at 373 K, in order to determine their structural and magnetic phase diagram. For high Mn content (x < 1) they form complex hydrides (deuterides) with y = 6 and crystallize in a cubic K₂PtCl₆ structure (Fm-3m space group). For 0.2 ≤ x < 1 the complex hydrides coexist with metal hydrides (y = 5) crystallizing in a cubic MgCu₂ type structure (Fd-3m space group). Single phase hydrides with MgCu₂ type structure are obtained for 1 ≤ x ≤ 1.5 with interstitial H(D) atoms localized in tetrahedral Y₂(Mn,Fe)₂ sites (y = 5). The cubic cell volume decreases versus Fe content and is 1.4% larger for the hydride compared to the corresponding deuteride. For x > 1.5 the compounds display an orthorhombic distortion (Pmn₁ space group) which is due to H or D ordering in 8 interstitial sites. The magnetic measurements of hydrides and deuterides show a decrease of the magnetization compared to their parent compounds whereas a large irreversibility is observed below the magnetic ordering temperature which depends on the Fe content. Neutron diffraction measurements at 2 and 300 K reveal the existence of only short range order magnetic interactions.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

RFe₂ and RMn₂ compounds (R = Y, rare-earth) have been studied for their interesting magnetic properties. Giant magnetostriuctive effects have been discovered in these compounds, particularly for R = Tb and Dy, and magnetostriuctive actuators based on RFe₂ compounds have been developed for so called Terfenol compounds [1–6]. Magnetic properties of these compounds can be tuned by hydrogen absorption through both the cell volume variation and the density of state modulation due to the addition of hydrogen electrons [7]. The structural and magnetic properties of RMn₂H₃ and RFe₂H₄ hydrides have been therefore widely studied showing interesting and complex structural and magnetic phase diagrams [8–16]. A strong interplay has been observed between the structural modifications induced by the ordering of interstitial hydrogen atoms inside the lattice and the magnetic order. In this work we will focus on YMn₂₋ₓFeₓ hydrides and deuterides to observe the influence of H absorption on the transition metal sublattice as Y is a non-magnetic element.

YMn₂ crystallizes in MgCu₂ type cubic structure and is helimagnetic below TN = 100 K, with strong spin fluctuations above TN [17–21]. The pyrochlore arrangement of the Mn sublattice induces a strong frustration between the Mn moments. Hydrogen absorption in YMn₂ leads to a lowering of crystal symmetry which releases the frustration and a coincidence is observed between the structural and magnetic transition temperatures in YMn₂Hₓ hydrides (0.1 ≤ y ≤ 4.5) [22–26]. The increase of TN versus H content is related to the cell volume increase, i.e. to the enlargement of the Mn-Mn distances. YMn₂H₄.₅ is rhombohedral and antiferromagnetic below 360 K [11,27]. Hydrogen absorption in YFe₂ (1.2 ≤ y ≤ 4.2) yields to the formation of several phases with different structures derived from the MgCu₂ cubic structure of the parent compound due to deuterium ordering below a given order-disorder temperature [14,28]. For y ≤ 3.5, the compounds are ferromagnetic (FM), the Fe moment increases whereas the Curie temperature (TC) decreases versus the H content [29]. YFe₂H₄.₂ is monoclinic below 330 K and undergoes a sharp ferromagnetic-antiferromagnetic (FM-AFM) transition around the transition
temperature $T_{FM-AFM} = 130$ K [30]. In addition, $T_{FM-AFM}$ is very sensitive to any cell volume change induced by (H,D) isotope effect, applied pressure and chemical substitution [31,32]. It is interesting to note that H absorption has opposite effects on the transition temperatures in YMn$_2$ and YFe$_2$ [33].

We found that new hydrides with larger H content can be obtained by submitting YMn$_2$ and YFe$_2$ to high hydrogen pressure up to 1 GPa at 373 K. YMn$_2$ can absorb up to 6 H/f.u. to form a complex YMn$_2$H$_6$ hydride [34,35]. It crystallizes in a disordered fluorite structure (K$_2$PtcI$_6$ type) described in the Fm-3m space group (N° 225). In this structure, Y and half the Mn atoms (Mn1) occupy randomly the 8c site whereas the remaining Mn atoms (Mn2) are located in the 4a site being surrounded by 6 D atoms in the 24e site [35]. This structure is very different from that observed for the other interstitial YMn$_2$H$_6$ hydrides ($\gamma \leq 4.5$) and results from a complete reorganization of the unit cell of the parent compound. YMn$_2$D$_6$ is a magnetopramagnet which follows a modified Curie Weiss law.

The neutron powder diffraction (NPD) study has confirmed the absence of long range magnetic order from 1.5 to 290 K in YMn$_2$D$_6$. YFe$_2$ can absorb up to 5 H/f.u. and YFe$_2$H$_5$ crystallises into an orthorhombic structure derived from the parent cubic C15 structure [36]. YFe$_2$H$_5$ has a low magnetization independent of the temperature over and no ordered Fe moment. This was confirmed by Mössbauer experiments and explained by band structure calculation: the spin non polarized configuration becomes more stable than the polarized one due to strong Fe-H bonding [29,36].

Beside their interesting physical properties, it is worth to note that YFe$_2$ and YMn$_2$ can store a large amount of hydrogen (2.5–3 wt %), and could be also used as hydrogen storage materials if their hydrogenation properties are tuned by appropriate chemical substitutions. Recent work has shown that partial Al for Fe substitution in YFe$_2$ allows to absorb about 3 H/f.u. and obtain a reversible capacity of 1.4 wt% without disproportionation and a fast kinetic [37].

Owing to these original results, our purpose was therefore to investigate the structural and magnetic properties of the YMn$_{2-x}$Fe$_x$ hydrides (deuterides) synthesized under high hydrogen or deuterium pressure. Previous results were already obtained for $x = 0.2$ and $x = 1$. YMn$_{1.8}$FeO$_{2.2}$ crystallizes in the same structure as YMn$_2$D$_6$, with Fe substituted on the 4a site [38,39]. YMn$_{1+x}$FeD$_{3-x}$ crystallizes in the MgCu$_2$ structure with $a = 0.81350$ nm [40]. A hydride with larger H content YMn$_{1+x}$FeD$_{3-x}$ crystallizing in the same cubic structure with $a = 0.81893$ nm, was also observed but was unstable versus time and could not be characterized magnetically [40].

In the present work, we have extended these studies to the full Fe substitution range in order to determine the YMn$_{2-x}$Fe$_x$ hydrides (deuterides) structural and magnetic phase diagram for H (D) contents between 5 and 6 H(D)/f.u.. Our aim was first to search eventual new structures and to determine the boundary limits of each phase. The evolution of the magnetic structure was also studied by combining magnetic measurements and neutron diffraction experiments. These results will be discussed and compared with those of previous works.

2. Experimental

YMn$_{2-x}$Fe$_x$ intermetallic compounds ($x = 0, 0.2, 0.25, 0.5, 1.0, 1.25, 1.5, 1.75, 1.9, 2$) were prepared by induction melting of the pure elements (Y 99.9%; Mn and Fe 99.99%) followed by an annealing treatment of 15 days at 1073 K. The sample composition and homogeneity were checked by X-ray diffraction (XRD) and electron probe microanalysis (EPMA). The syntheses of YMn$_{2-x}$Fe$_x$ hydrides and deuterides were carried out at 0.9 GPa and 373 K using the high pressure device described in Refs. [41,42].

The XRD patterns were measured with a D8 Brucker diffractometer using the Cu K$_\alpha$ radiation.

The neutron powder diffraction (NPD) patterns of the deuterides have been registered at 300 K on the 3T2 high resolution spectrometer and at 1.8 K and 298 K on the G4.1 spectrometer at the Laboratoire Léon Brillouin (LBB) at Saclay. For the experiments on 3T2, the wavelength was 0.1225 nm and the angular range 6° $\leq 2\theta \leq 125°$ with a step of 0.05°. For the experiments on G4.1, the wavelength was 0.2427 nm and the angular range was 2° $\leq 2\theta \leq 82°$ with a step of 0.1°. The deuterides were contained in a vanadium sample holder.

All the XRD and NPD patterns were refined with the Rietveld method, using the Fullprof code [43]. The line shapes were refined with a Pearson VII function.

The magnetic measurements were performed with a Physical Properties Measurements System (PPMS) apparatus of Quantum Design operating up to 9 T (7161 kA/m) and from 1.5 to 300 K. Magnetic measurements were also performed on a MANICS DSM8 to determine the Curie temperatures above 300 K.

3. Results and discussion

3.1. Crystal structures

3.1.1. Intermetallic compounds

XRD and EPMA results on YMn$_2$–Fe$_x$ alloys are reported in Table 1. The samples with $x = 0.5$ and 1 contains some inclusions of YMn$_{2.5}$Fe$_{0.5}$, YMn$_{2.2}$Fe, La$_{0.2}$YMn$_{1.8}$Fe$_{0.2}$, and YMn$_{1.6}$Fe$_{0.4}$ [44]. The Rietveld analysis shows that the average composition is close to the nominal value, but with a slightly larger Mn content $x = 0.2$ and 0.5. All YMn$_{2-x}$Fe$_x$ compounds crystallize in the MgCu$_2$ type cubic structure (Fd-3m space group) with a disordered Fe for Mn substitution on 16d site. However, although a complete solid solution exists between YMn$_2$ and YFe$_2$, the evolution of the cell parameter versus Fe content is not linear, showing a deviation from the Vegard’s law (Fig. 1). The experimental data can be fitted with a second order polynomial fit:

$$a = 7.6743 - 0.236x + 0.397x^2 + V$$

$$V = 451.92 - 40.96x + 7.204x^2$$

(1)

This deviation indicates that we have not a pure geometric dilution. The calculation of the interatomic distances using the cell parameters leads to $d_{Mn-Mn} = 0.2715$ nm in YMn$_2$ and $d_{Fe-Fe} = 0.2602$ nm in YFe$_2$ which difference is quite large taking into account the different atomic radii of Mn and Fe atoms. Yoshimura et al. [44] have also found that the cell parameters of YMn$_2$–Fe$_x$ alloys are smaller than expected from Vegard’s law for even small Fe content ($x \leq 0.4$). They observed by $^{55}$Mn NMR (Nuclear Magnetic Resonance) that a small Fe for Mn substitution ($x = 0.16$) leads to a collapse of the Mn moments and a sharp decrease of $T_N$ [44]. The large decrease of the volume ($5\%$) at $T_N$, related to the localization of the Mn moments in YMn$_2$ disappears upon Fe substitution. Above $T_N$, YMn$_2$ displays a large thermal expansion coefficient which has been explained by magnetovolume effects arising from the excitation of the spin fluctuations in the paramagnetic state [45]. Rainford et al. [46] showed by muon spin relaxation ($\mu$SR) studies a slowing down of the dynamical fluctuations upon Mn for Fe substitution. Note that this suppression of spin fluctuation is also observed when applying an hydrostatic pressure, showing the influence of the reduction of the Mn-Mn distances [47]. Therefore, the deviation from the Vegard’s law can be attributed to a progressive reduction of the spin fluctuations upon Fe for Mn substitution, leading to a reduction of the thermal expansion coefficient [48] and consequently to a larger cell volume decrease at room temperature.
3.1.2. Hydrides and deuterides

XRD patterns of the YMn2–xFex hydrides are compared in Fig. 2 and the results of Rietveld refinements for both hydrides and deuterides reported in Table 2. These compounds crystallize in three different types of structure depending on the Fe content: cubic K2PtCl6 type, cubic MgCu2 type and orthorhombic ErFe2D5 type. No other type of structure has been observed. Small amount of Y6Mn23–xFe2x hydrides were observed for x = 0.5 and 1 due to the hydrogenation of the second phase. For the phases with K2PtCl6 structure type, the H(D) content is fixed to 6, as H atoms form complex MnH6 octahedra. The interstitial hydrogen (deuterium) content was estimated around 5 H(D)/f.u. for the cubic MgCu2 structure, according to previous estimations from cell volume variation and this content is determined below by neutron diffraction analysis on selected deuterides. The deuterium content in the orthorhombic structure has been previously determined for isostructural ErFe2D5 compound [49]. The reduced cell volume V/Z and the weight percentage (wt%) of each phase are represented versus H(D) content in Fig. 3.

The analysis of the XRD patterns shows that hydrides (deuterides) with cubic K2PtCl6 type structure are observed for 0 < x < 0.5 and with orthorhombic structure for 1.75 < x < 2. A two phase range with the coexistence of the two types of cubic structure (K2PtCl6 and MgCu2) is therefore observed for 0.2 < x < 1.5. The compounds with 1 < x < 1.5 are single phase with cubic MgCu2 structure. A mixture of cubic MgCu2 and orthorhombic phase is observed for x = 1.75. The cell volume of cubic MgCu2 hydrides decreases linearly versus Fe content.

For a given Fe content, the reduced cell volume V/Z is significantly larger for the complex hydrides (deuterides) YMn2–xFe1–xHx compared to the cubic interstitial hydrides (deuterides) YMn2–xFe1–xH(D)x (Fig. 3). However, the calculation of (ΔV/V)/y ratio gives a value between 5.6 and 6.2 for the hydrides whatever the Fe content and the structure, showing that the relative cell volume increase is proportional to the H content. These calculated ratios are slightly but systematically smaller for the cubic interstitial deuterides, i.e. between 5.4 and 5.8, showing an H, D isotope influence.
Indeed, a larger cell volume is observed for the hydrides compared to the deuterides with MgCu₂ type structure ((V_H/C₀VD)/VD = 1.4%). This cell volume difference can be attributed to the larger zero point amplitude of vibration of interstitial hydrogen compared to deuterium and is even larger than that observed for the YFe₂(H,D)₄.2 compounds ((V_H/C₀VD)/VD = 0.8%) [30]. On the contrary, the complex hydrides and deuterides are not very sensitive to the D for H substitution, showing that the M-H and M-D covalent bonding are not so isotope sensitive.

In order to determine the D atom sites and their occupancy number in the compounds with cubic MgCu₂ structure, neutron diffraction experiments were performed on 3T2 at 300 K on YMn₂ₓFeₓHₓ compounds with x = 1 and 1.5 and also at 2 K for x = 1.5. The NPD patterns refined in Fd-3m space group are displayed in Fig. 4 and the analysis results are reported in Table 3.

For both compounds the occupancy numbers of Mn and Fe are in relative agreement with the analyzed composition (x = 1.6 rather than 1.5 for the second compound). The D atoms are located in tetrahedral Y₂M₂ sites (32e) were found empty. This corresponds to a disordered structure, where the D atoms are statistically distributed in 5 over 12 possible Y₂M₂ sites/f.u.. The bump centered at 2 theta = 37° corresponding to an interplanar distance d = 0.21 nm in the background of NPD patterns is characteristic of short range order due to the existence of close D-D atoms separated by about 0.21 nm, which is often observed in deuterium rich interstitial

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cubic</th>
<th>K₂PtCl₆</th>
<th>Cubic</th>
<th>MgCu₂</th>
<th>Orthorhombic</th>
</tr>
</thead>
<tbody>
<tr>
<td>YMn₂H₆</td>
<td>0.6706(9)</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>YMn₂D₆</td>
<td>0.6709(1)</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>YMn₁.9Fe₀.06H₆</td>
<td>0.6715(6)</td>
<td>80.5</td>
<td>0.8269(1)</td>
<td>19.5</td>
<td></td>
</tr>
<tr>
<td>YMn₁.9Fe₀.06D₆</td>
<td>0.6708(2)</td>
<td>77.8</td>
<td>0.830(3)</td>
<td>22.2</td>
<td></td>
</tr>
<tr>
<td>YMn₁.9Fe₀.06H₂</td>
<td>0.6686(2)</td>
<td>55.8</td>
<td>0.8204(1)</td>
<td>44.2</td>
<td></td>
</tr>
<tr>
<td>YMn₁.9Fe₀.06D₂</td>
<td>0.6172(3)</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>YMn₁.9Fe₀.06H₃</td>
<td>0.8130(1)</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>YMn₁.9Fe₀.06D₃</td>
<td>0.8067(1)</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>YMn₁.9Fe₁.5₁H₄</td>
<td>0.80685(4)</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>YMn₁.9Fe₁.5₁D₄</td>
<td>0.8027(1)</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>YMn₁.9Fe₁.6₅H₅</td>
<td>0.80053(1)</td>
<td>17.3</td>
<td>a = 0.5503(3) b = 0.5832(3) c = 0.80873(5)</td>
<td>82.7</td>
<td>27.4/28.9</td>
</tr>
<tr>
<td>YMn₀.₇₅Fe₁.₂₅D₅</td>
<td>0.8064(2)</td>
<td>100</td>
<td>a = 0.54434(2) b = 0.58448(2) c = 0.80800(2)</td>
<td>100</td>
<td>28.9</td>
</tr>
<tr>
<td>YMn₀.₅₁Fe₁.₅₄D₅</td>
<td>0.80675(1)</td>
<td>100</td>
<td>a = 0.54369(2) b = 0.58498(2) c = 0.80821(2)</td>
<td>100</td>
<td>28.9</td>
</tr>
<tr>
<td>YMn₀.₃₂Fe₁.₆₈H₅</td>
<td>0.80053(1)</td>
<td>17.3</td>
<td>a = 0.5503(3) b = 0.5832(3) c = 0.80873(5)</td>
<td>82.7</td>
<td>27.4/28.9</td>
</tr>
<tr>
<td>YMn₀.₁₀Fe₁.₉₂H₅</td>
<td>0.8064(2)</td>
<td>100</td>
<td>a = 0.54434(2) b = 0.58448(2) c = 0.80800(2)</td>
<td>100</td>
<td>28.9</td>
</tr>
<tr>
<td>YFe₁.₉₈H₅</td>
<td>0.8064(2)</td>
<td>100</td>
<td>a = 0.54434(2) b = 0.58448(2) c = 0.80800(2)</td>
<td>100</td>
<td>28.9</td>
</tr>
</tbody>
</table>

* Phase 1 corresponds to the cubic K₂PtCl₆ phase for x < 1 and the MgCu₂ phase for x = 1.68, phase 2 corresponds to the MgCu₂ phase for x < 1 and the orthorhombic phase for x = 1.68.
deuterides [50]. The NPD pattern of YMn0.5Fe1.5D5 at 2 K can be refined in the same structure than at 300 K, with a cell volume contraction. Therefore, we can conclude that no change of the crystal symmetry occurs at low temperature.

This structural analysis shows that the YMn2−xFex hydrides or deuterides can crystallize in a complex fluorite structure for a limited range of Fe for Mn substitution with 0 < x < 1. Previous NPD results have shown that Fe substitutes to Mn only on the 4y site because of both geometric and electronic properties [39]. The preferential substitution on 4y site stabilizes the orthorhombic structure is more stable than the cubic one with a cell parameter increase of 8% and an H content estimated between 3.7 and 4 H/f.u.. In the work of Cadavez-Peres et al.[55] deuterides can crystallize in a complex crystalline structure corresponding to a disordered MgCu2 type phase diagram, but also for Y-Mn alloys with different Y/Mn stoichiometry [40,58]. As Y and Mn contents are changing, the stability of the YMn2−xFex hydrides or deuteride, probably related to different electronic configuration. Indeed, it has been observed that Mn0.5H2 type complex hydrides can be obtained for various rare earth (R = Er, Ho, Dy, Gd) starting from either cubic or hexagonal Laves phase compound, but also for Y-Mn alloys with different Y/Mn stoichiometry (Y6Mn2 or YMn12) [56–58]. On the other hand ErFeMnH5 and ErFexH5 hydrides crystallize in the same cubic MgCu2 and orthorhombic structures respectively than the same compounds with Y [40,58]. As Y and R have the different metallic radius but the same number of valence electrons this confirms that the electronic criteria is more important than the geometric one (in a reasonable limit) for the stability of the hydride structure.

### 3.2. Magnetic properties

#### 3.2.1. Intermetallic compounds

The transition temperatures and saturation magnetizations were obtained from magnetic measurements of all YMn2−xFex intermetallic compounds. The magnetization curves of YMn1.5Fe0.5 are reported as an example (Fig. 5). The analysis of the slope of the magnetization curves in the paramagnetic range gives a Curie constant C = 0.35 emu/mol, an effective moment μeff = 1.68 μB and a negative paramagnetic temperature Tp = −19.3 K characteristic of an antiferromagnetic behaviour (AFM). The zero-field cooled (ZFC) and field cooled (FC) curves are different below the Neél temperature TN = 5 K, indicating a small irreversibility in this compound, probably due to a spin glass behaviour. The analysis of the magnetization curves shows that the intermetallics with x ≤ 0.5 display an antiferromagnetic behaviour (AFM) below TN whereas a ferromagnetic (FM) behaviour is observed for x > 0.5, with an almost linear increase of TC versus Fe content (Fig. 6). The spontaneous magnetizations (M0) were extrapolated from the M(H) curves at high field at 2 K and 300 K (Fig. 6). A sharp increase of M0 is observed versus Fe content above x = 0.5 at 2 K and x = 1 at 300 K. These results are in agreement with those published in Refs. [59,60], in which a critical change of the magnetic order was observed at x = 0.5.

Several authors have tried to determine the evolution of the Fe and Mn moments in YMn2−xFex versus x, using experimental results and theoretical calculations [60–65] and quite different results were obtained. The Mn moment in YMn2 is 2.7 μB, in a helimagnetic structure close to an AFM arrangement. In VFe2, the Fe

### Table 3

<table>
<thead>
<tr>
<th>Deuterides</th>
<th>YMnFeD5</th>
<th>YMn0.5Fe1.5D5</th>
<th>YMn0.5Fe1.5D5</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (K)</td>
<td>300</td>
<td>300</td>
<td>2</td>
</tr>
<tr>
<td>a (nm)</td>
<td>0.8127(1)</td>
<td>0.80362(1)</td>
<td>0.8019(1)</td>
</tr>
<tr>
<td>V (nm³)</td>
<td>0.5380(1)</td>
<td>0.51898(1)</td>
<td>0.5167(1)</td>
</tr>
<tr>
<td>n(H/f.u.)</td>
<td>0.987(4)</td>
<td>0.416(1)</td>
<td>0.40(1)</td>
</tr>
<tr>
<td>n(H/f.u.)</td>
<td>1.013(4)</td>
<td>1.584(1)</td>
<td>1.60(1)</td>
</tr>
<tr>
<td>D position</td>
<td>96 x(x,y,z)</td>
<td>0.3295(7)x</td>
<td>0.3308(1)</td>
</tr>
<tr>
<td>Y2M2 site</td>
<td>0.138(2)</td>
<td>0.140(2)</td>
<td>0.1391(2)</td>
</tr>
<tr>
<td>y (nD/f.u.)</td>
<td>5.11(4)</td>
<td>5.03(4)</td>
<td>5.00(6)</td>
</tr>
<tr>
<td>B (Y)</td>
<td>1.30(3)</td>
<td>1.67(3)</td>
<td>1.68(5)</td>
</tr>
<tr>
<td>B (Mn, Fe)</td>
<td>1.29(3)</td>
<td>1.28(2)</td>
<td>1.05(3)</td>
</tr>
<tr>
<td>B (D)</td>
<td>2.88(4)</td>
<td>3.21(5)</td>
<td>2.87(6)</td>
</tr>
<tr>
<td>χm(T)</td>
<td>3.80</td>
<td>8.25</td>
<td>11.5</td>
</tr>
<tr>
<td>Rexp (%)</td>
<td>13.1</td>
<td>12.4</td>
<td>14.0</td>
</tr>
<tr>
<td>Rexp (%)</td>
<td>9.25</td>
<td>7.29</td>
<td>6.69</td>
</tr>
</tbody>
</table>
calculated the electronic structure of a Mn$_4$Y$_4$Fe$_{12}$Y$_6$ cluster, interpreting, 55Mn and 89Y NMR, 57Fe Mössbauer experiments. Using $^{89}$Y NMR spectra, Nagai et al. [61] proposed that the Fe moments remain almost constant and there are two types of Mn moments, coupled either parallel to Fe with $M_{\text{Mn}} = 0.6 \mu_B$ or antiparallel with $M_{\text{Mn}} = 2.8 \mu_B$. Besnus et al. [60] interpreted their experimental results (Diffuse Neutron scattering, $^{55}$Mn and $^{89}$Y NMR, $^{57}$Fe Mössbauer spectroscopy) by a ferromagnetic coupling of Fe and Mn moments, a strong decrease of Fe moment and a smaller variation of Mn moments as $x$ decreases. From first-principles self consistent field calculations, J.W Cai et al. [64,65] calculated the electronic structure of a Mn$_2$Y$_4$Fe$_{12}$Y$_6$ cluster, and found that when the Fe atom has one Mn neighbor, its moment decreases and the Mn moment is 0.71 $\mu_B$ and parallel to the Fe moment. The difficulty to have a clear microscopic description of the intensity and orientation of the Fe and Mn moments should be related to the chemical disorder with a statistical distribution of Fe and Mn atoms on the same Wyckoff site, which prevents any long range order and may induce a distribution of the transition metal moments.

3.2.2. Hydrides and deuterides

The magnetic properties of YMn$_2$H$_x$D$_{1-x}$, YMn$_{1.8}$Fe$_{0.2}$H$_x$D$_{1-x}$, YFeMn$_x$H$_3$ and YFe$_2$H$_5$ compounds have been already published in Refs. [35,36,39,40]. Additional magnetic measurements have been performed in this study for $x = 0.5, 1.5, 1.75$ and 1.9.

The ZFC and FC magnetization curves versus temperature measured under an applied field 23.87 kA/m (for $x = 0.5$ a FC curve was only measured down and up) are presented in the left part of Fig. 6. From first-principles self consistent field calculations, J.W Cai et al. [64,65] calculated the electronic structure of a Mn$_2$Y$_4$Fe$_{12}$Y$_6$ cluster, and found that when the Fe atom has one Mn neighbor, its moment decreases and the Mn moment is 0.71 $\mu_B$ and parallel to the Fe moment. The difficulty to have a clear microscopic description of the intensity and orientation of the Fe and Mn moments should be related to the chemical disorder with a statistical distribution of Fe and Mn atoms on the same Wyckoff site, which prevents any long range order and may induce a distribution of the transition metal moments.

The ZFC and FC magnetization curves versus temperature with $H = 23.87$ kA/m (a) and isothermal magnetization curves versus applied field (b) of YMn$_{1.5}$Fe$_{0.5}$ are presented in Fig. 5. For all samples the FC magnetization increases upon cooling and the ordering temperature varies between 160 and 295 K, but not in a regular way versus $x$ content (Fig. 8a). In addition, a difference has been observed between the ZFC and FC curves below a blocking temperature $T_B$ and a maximum of the ZFC curve at $T_{\text{max}}$ is observed below $T_B$. This low temperature irreversibility suggests that spin glass behaviour can occur for these intermediate YMn$_2$$_x$Fe$_{1-x}$D$_5$ compounds. For memory, YMn$_2$D$_5$ displays a modified Curie Weiss behaviour and YFe$_2$H$_5$ is a Pauli paramagnet.

The evolution of the transition temperatures of the hydrides (deuterides) is compared with those of the parent compounds in Fig. 8a. This transition temperature is larger for the hydride (deuteride) than for their parent compounds when $x \leq 1$ and become smaller for larger $H$ ($D$) content.

The magnetizations versus field were measured at different temperatures between 2 and 300 K (Fig. 7, right). The comparison of the curves at 2 K shows that the saturation is not completely reached at 9 T for all samples, but the slope becomes smaller as $x$ increases. If we assume that this is a signature of the competition between antiferromagnetic and ferromagnetic interactions, it means that the ferromagnetic interactions become larger as the Fe content increases. The values of $M_s$ were extrapolated from the $M(H)$ curves at high field (Fig. 8b). At 2 K the tendency is an increase of $M_s$ versus Fe content up to $x = 1.5$ when the hydrides (deuterides) are cubic. Then in the presence of the orthorhombic phase the moment remains around 1.5 $\mu_B$ and decrease to 1 $\mu_B$ for $x = 2$. The $M_s$ values of hydrides and deuterides are always smaller than those of their parent compounds for the same $x$ value. At 300 K, the samples are in paramagnetic state and $M_s$ remains smaller than 0.2 $\mu_B$.

The NPD patterns of YMnFeD$_5$ and YMn$_{0.5}$Fe$_{1.5}$D$_5$ were measured at 1.8 K and 300 K on G4.1 spectrometer in order to check the existence of possible long range magnetic order. The comparison of the NPD patterns of YMn$_2$$_x$Fe$_{1-x}$D$_5$ (Fig. 9) and YMnFeD$_5$ measured at 1.8 and 300 K on G4.1 shows mainly a raise of the background at low angle and a shift of the peak positions due to a cell volume contraction. The absence of additional Bragg peak or significant change of peak intensity reveals the absence of long range magnetic order in these deuterides. The background increase at 2 K compared to that at 300 K can be related to short range order ferromagnetic correlations as observed for RMn$_2$$_x$Fe$_{1-x}$D$_5$ complex deuterides [39,56,57].

These magnetic results can be compared with those of Okamoto et al. [54] which were measured by a vibrating sample magnetometer and Mössbauer experiments. In YMn$_2$$_x$Fe$_{1.7}$H$_{4.0}$ compounds ($x = 1.2$–$2$) the Curie temperatures were smaller than for the parent compounds whereas the saturation magnetization at 4.2 K were larger than the parent compound for $x = 1.4$, and lower for larger Mn content. In addition both $T_C$ and $M_s$ decrease upon Mn for Fe substitution.
The analysis of the magnetic properties of YMn$_2$Fe$_x$D$_{4.3}$ deuterides by neutron diffraction [55] showed below what was called critical temperature $T_{\text{Crit}}$, the existence of a short range magnetic order (SRO) with a crossover from antiferromagnetic SRO towards ferromagnetic SRO with an incommensurate behaviour in the intermediate range. The $k$ propagation vector decreases linearly from $(1/2,1/2,1/2)$ for $x=0.3$ towards $(0,0,0)$ for $x=1.2$. The correlation length decreases from 1.5 to 0.5 nm for $x=0.2$ to 0.4 and increases again above $x=1.2$ reaching 3 nm. This evolution of the magnetic structure was attributed to the competition of the Mn-Mn, Mn-Fe and Fe-Fe interactions.

Although the magnetic properties of YMn$_2$Fe$_x$D$_{y}$ deuterides were not investigated for all samples by the same methods in this previous work ($y=4.3$) and the present one ($5 \leq y \leq 6$), it appears that in both systems only SRO exists and results from a local competition of AFM and FM interactions. A clear difference concerns the so called $T_{\text{Crit}}$ in Ref. [55] and magnetic ordering temperature observed in this work. In YMn$_2$Fe$_x$D$_4$ $T_{\text{Crit}}$ remains elevated: around 340–360 K for $x=0$ and 2, and it increases linearly between 210 K and 250 K for $x=0.2$ to 1.7. For YMn$_2$Fe$_x$H$_{5-6}$ there is no ordering temperature for $x=0$ and 2, whereas an ordering temperature which varies non linearly versus $x$, is observed for intermediate $x$ content. The tendency to change from AFM towards FM order can be deduced from the shape of the $M(H)$ curves and the increase of $M_S$ versus $x$ content.

Fig. 7. Magnetization curves of YMn$_{2-x}$Fe$_x$H(D)$_5$ compounds versus temperature with $H=23.87$ kA/m (left) and applied field (right) at various temperature. For $x=1$ and 1.5 the samples are those used for NPD experiments.
properties shows that there is only a short range magnetic order in the
curve.

4. Conclusions

The crystal structure and magnetic phase diagram of $\text{YN}_{1-x} \text{Fe}_{x} \text{H}_{6.5}$ compounds synthesized at high pressure has been determined. Three different structural behaviours were observed: cubic $\text{K}_{2} \text{PcCl}_{6}$ type for the Mn rich side, cubic MgCu$_2$ type structure with H(D) atoms in $\text{A}_2 \text{B}_2$ sites for the intermediate range and orthorhombic for the Fe rich side. An (H,D) isotope effect has been observed between the cell volume of the disordered cubic hydrides and deuterides ($0.1 \leq x \leq 1.55$). The study of the magnetic properties shows that there is only a short range magnetic order in the hydrides and deuterides, an increase of the magnetization below $T_C$ for intermediate Fe content, as well as an increase of the saturation magnetization at 2 K as $x$ increases. This can be related to a competition between FM and AFM magnetic local interactions. Further studies will be performed using $^{57}$Fe Mössbauer spectroscopy to observe the evolution of the local magnetic order on Fe sites. The influence of the substitution of Y by a magnetic rare-earth (Dy, Er) will be also investigated more systematically.

Acknowledgments

We are thankful to G. André and F. Porcher for their help to perform the neutron diffraction experiment as local contacts and to the Laboratoire Léon Brillouin (LLB) to provide us for neutron beam time. Some compounds presented in this work have been studied by A. N’Daye during his research training work in the laboratory.

References

[14] D. Fruchtar, Y. Berthier, T. de Saxce, P. Valliut, Effects of rhombohedral distortion on the magnetic properties of $\text{YFe}_2\text{H}_4$ hydrides (R = Tm, Er), J. Less Common Met. 130 (1987) 89–95.
[30] V. Paul-Boncour, M. Guillot, C. Wiesinger, G. André, Giant isotropic effect on

31. T. Leblond, V. Paul-Boncour, M. Guillot, Large (H,D) isoote effect on the
magnetictransition in Y0.98Fe2.05Hx.5D4.5, Compounds. J. Appl. Phys. 99 (2006) 085005.

K. Yoshimura, M. Takigawa, H. Yasuoka, M. Shiga, Y. Nakamura, Spin

33. V. Paul-Boncour, Comparison of the influence of hydrogen on the magnetic

34. C.-Y. Wang, V. Paul-Boncour, R.-S. Liu, A. Percheron-Gu
M. Shiga, Magnetism and spin

35. V. Paul-Boncour, S.M. Filipek, I. Marchuk, G. Andr
G. Andr