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Origin of the first order magnetostructural transition in $YFe_2D_{4.2}$

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Abstract

The deuterium order–disorder and the first order magnetic transitions in $YFe_2D_{4.2}$ have been studied by X-ray and neutron diffraction, magnetization measurements and ^{57}Fe Mössbauer spectroscopy. From 363 down to 290 K, a progressive lowering of the crystal symmetry from cubic to rhombohedral and then monoclinic structure is observed. At 290 K $YFe_2D_{4.2}$ crystallizes in a primitive monoclinic space group P1c with $a = 9.429(1)$ Å, $b = 11.474(1)$ Å, $c = 5.508(1)$ Å, $\beta = 122.37^\circ$. This lowering of crystal symmetry leads to very different quantity of D neighbours around each Fe sites. The magnetic study shows that the moment of the Fe3 atoms, surrounded by nearly 5 D atoms, collapses at 84 K, leading to a transition from a ferromagnetic to an antiferromagnetic structure. The first order transition at 84 K is associated with a 0.55% volume decrease and the magnetization curves above 84 K display the same behaviour than the collective electron metamagnetism (CEM) observed in RCo_2 compounds. This is related to the fact that for critical deuterium content between 4 and 5 D atoms in YFe_2 the Fe 3d ferromagnetism becomes instable due to a strong modification of the electronic band structure.

Keywords: Hydrogen storage materials; X-ray diffraction; Neutron diffraction; Magnetic measurements; Mössbauer spectroscopy

1. Introduction

The study of the YFe_2D_x system has shown that deuterides with various deuterium content can be prepared from $x = 1.3$ to 5 D/f.u. [1–4]. At room temperature these deuterides display a large variety of crystal structures related to a lowering of the cubic C15 symmetry of YFe_2 which are due to a preferential order of the deuterium atoms in the interstitial sites below a critical temperature T_S [5]. From $x = 1.3$ to 3.5 the deuterides are characterized by a linear decrease of the Curie temperature T_C and a progressive increases of the Fe moment [1,5]. For $x = 4.2$, the compound is ferromagnetic up to 90 K, then display a sharp decrease of the magnetization through a first order transition [6]. For $x = 5$ there is no more ordered Fe moment [4]. These results indicate that between $x = 3.5$ and 5 the ferromagnetism of the Fe moment become unstable due to the strong influence of the deuterium atoms on the electronic structure [7]. In addition, a previous work has showed that for $x = 4.2$ the magnetic properties becomes very sensitive to the H/D isotopic effect, i.e. the first order magnetic transition is shifted from 90 to 140 K when the deuterium is substituted by hydrogen atoms [6]. In the present study we will report extended experimental results compared to those published in Ref. [6]. In order to understand the origin of this first order transition in $YFe_2D_{4.2}$ the structural and magnetic properties of $YFe_2D_{4.2}$ will be investigated by X-ray (XRD) and neutron powder diffraction (NPD), high magnetic field measurements and ^{57}Fe Mössbauer spectroscopy.

2. Experimental

The preparation and characterization of single phase YFe_2 and its deuterides is described in [6]. X-ray diffraction (XRD) measurements were done using a Bruker D8 diffractometer

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(Cu Kα radiation). An XRD pattern of $YFe_2D_{4.2}$ at 290 K was also measured using synchrotron radiation ($\lambda = 0.74744$ Å) provided on the Swiss-Norwegian beam line at the ESRF (Grenoble). The NPD experiments were performed at the LLB (Saclay), using the 3T2 and G4.1 diffractometers. The wavelengths were 1.2251 and 2.4266 Å, respectively. The magnetization measurements were performed using a high-magnetic field magnetometer ($B \leq 23$ T) at the LCMI (Grenoble). The ^{57}Fe Mössbauer spectra were recorded between 4.2 and 300 K using a conventional constant acceleration type spectrometer. The data were analyzed by superposing a set of discrete Lorentzians with equal width. The quadrupole interaction was treated as a perturbation to the magnetic hyperfine interaction. The isomer shift data are given relative to the source (Fe(Rh)).

3. Results

The analysis of the XRD and NPD patterns indicates that two different transitions occur in different ranges of temperature: around room temperature (363 down to 280 K) there is an order–disorder transition due to the ordering of D atoms. No significant change is observed from 280 down to 160 K. Then from 150 down to 1.5 K the evolution of the patterns is related to different magnetic transitions. These two parts will be presented separately, starting from the highest symmetry towards the lower one: i.e. with decreasing temperature for the D disorder-order transition and with increasing temperature for the magnetic order.

3.1. Deuterium order–disorder transition

The evolution of the NPD pattern of $YFe_2D_{4.2}$ measured on the G4.1 spectrometer indicates a lowering of the crystal symmetry as the temperature (T) decreases from 363 to 298 K. At 363 K the symmetry is cubic described by the Fd-3m space group ($a = 7.95$ Å) with deuterium atoms in both A2B2 ($x_D = 3.8$ D/f.u.) and AB3 sites ($x_D = 0.7$ D/f.u.). Below 340 K a rhombohedral distortion occurs and the pattern is refined in a rhombohedral space group with $a = 5.702$ and $c = 13.403$ Å. As T decreases the rhombohedral distortion increases. At 295 K the XRD pattern measured by synchrotron radiation (Fig. 1) reveals an additional splitting of the lines due to the formation of a monoclinic structure described by the space group $C2/m$ with $a = 9.429(1)$ Å, $b = 5.737(1)$ Å, $c = 5.508(1)$ Å, $\beta = 122.37°$ where b has the same value as the corresponding parameter a in the rhombohedral description ($a = 5.737(1)$ and $c = 13.220(1)$ Å). In this centred monoclinic structure there is one Y site (4i) and three Fe sites (2d, 2b, 4f).

The corresponding NPD pattern measured on 3T2 at 300 K displays additional lines which can be refined using the primitive space group $P21/a$ (Fig. 2 and Table 1). In this description

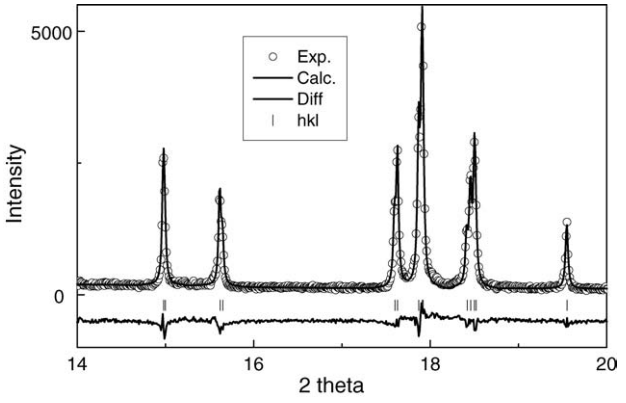

Fig. 1. XRD pattern of $YFe_2D_{4.2}$ measured with synchrotron radiation and refined in the $C2/m$ monoclinic space group.

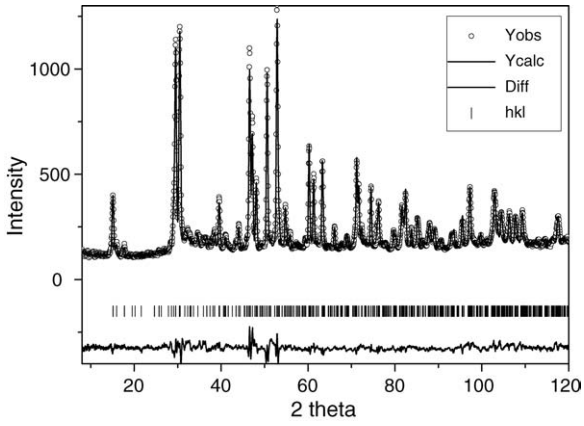

Fig. 2. Refinement of the NPD pattern of $YFe_2D_{4.2}$ at 290 K measured on 3T2 spectrometer in the monoclinic structure ($P21/a$) reported in Table 1.

The corresponding NPD pattern measured on 3T2 at 300 K displays additional lines which can be refined using the primitive space group $P21/a$ (Fig. 2 and Table 1). In this description

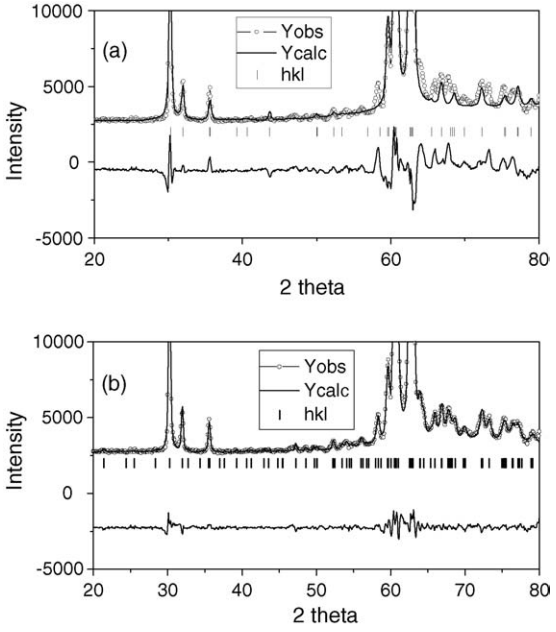

Fig. 3. NPD pattern of $YFe_2D_{4.2}$ measured at 290 K on G4.1 spectrometer refined (a) with the structure described in Table 1 and (b) in a pattern matching mode with a doubling of the b.