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Journal of Alloys and Compounds 262–263 (1997) 45–48

Journal of ALLOYS AND COMPOUNDS

Local structural and magnetic properties of YFe_2D_x compounds ($0 < x \leq 3.5$)

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Abstract

The local order in YFe_2D_x deuterides, which crystallize in different crystal structures derived from the C15 cubic structure are characterized by EXAFS and ^{57}Fe Mössbauer spectroscopy. For all the deuterides different Fe sites and a large distribution of Fe–Fe distances are observed, whereas around the Y atoms the distances are close to what is expected in the cubic C15 structure. The origin of the structural distortions is discussed in relation to the magnetic properties. © 1997 Elsevier Science S.A.

Keywords: Hydride; Structure; Magnetism; EXAFS; Mössbauer

1. Introduction

Intermetallic compounds of rare earths and transition metals have been studied for several years for their hydrogen storage properties which lead to various applications. From this perspective a good knowledge of the structural and electronic properties of these hydrides is necessary.

Among these compounds the RFe_2 hydrides are known to display a multi-plateau behaviour in their pressure composition isotherms [1,2]. For a long time, such thermodynamic behaviour remained unclear. The study of the YFe_2D_x compounds [3,4] has shown that a correlation can be established between this multi-plateau behaviour and the formation of several hydrides with different structures derived from the C15 cubic one. Several two-phase ranges are observed in agreement with the different plateaus of the isotherms. The symmetry and cell parameters of the deuterides have been determined by X-ray diffraction (XRD) at room temperature [3]. $YFe_2D_{1.2}$ and $YFe_2D_{1.9}$ display a tetragonal distortion ($a = 11.98$ Å, $c = 7.61$ Å and $a = 12.15$ Å, $c = 23.07$ Å, respectively). $YFe_2D_{1.75}$ has a cubic centered structure with a doubling of the cell parameter ($a = 15.34$ Å). The XRD patterns of YFe_2D_x compounds with $1.9 < x < 3.0$ are refined in the cubic C15 structure and those with $3.3 \leq x \leq 3.5$ in a rhombohedral structure ($a = 5.63$ Å and $c = 13.34$ Å).

YFe_2 is ferromagnetic with a Curie temperature of 560 K. The deuterides are still ferromagnetic with a rise of the total magnetic moment from 3 to 3.7 μ_B as the deuterium content increases from 1.2 to 3.5 D/f.u. A decrease of the Curie temperature is also observed which reaches 345 K for $x = 3.5$ [5].

In order to clarify the origin of the distortions, single phase deuterides ($1.2 \leq x \leq 3.5$) have been characterized both by Extended X-ray Absorption Fine Structure (EXAFS) and by ^{57}Fe Mössbauer spectroscopy, which probe for local order.

2. Experimental

The deuterides were prepared by deuterium absorption at 408 K for $1.2 \leq x \leq 3.3$ and at 300 K for

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PII S0925-8388(97)00327-7

$x = 3.5$ as described in [3]. The X-ray absorption experiments were performed at 10 K and at 300 K using the synchrotron radiation provided by the DCI ring at LURE. The EXAFS spectra were recorded at the Fe–K and Y–K edges on the EXAFS 2 spectrometer. The ^{57}Fe Mössbauer data were recorded at 4.2 K using a conventional transmission spectrometer.

3. Results

3.1. EXAFS

The EXAFS spectra of YFe_2D_x samples with $x = 0$, 1.2, 1.9, 2.5, 2.9 and 3.5 were analyzed using the program of D. Bonnin et al. [6].

At the Y edge (Fig. 1), the radial distribution function (RDF) of YFe_2 displays a peak located at approx. 2.8 Å, which can be attributed to the first Fe and Y shells. Increasing the deuterium content leads to a decrease of its intensity and a shift to larger distances. This peak was filtered between 1.9 and 3.7 Å, back-Fourier transformed and fitted using the theoretical functions of Mc Kale [7]. According to the cubic C15 structure each Y atom is surrounded by 12 Fe atoms and 4 Y atoms. Assuming that, in spite of the structural distortions, these mean coordination numbers remain unchanged for all the deuterides, it was possible to fit all the data correctly. The magnitude of the simulated interatomic distances increases with deuterium content (Fig. 2a) and are in good agreement with the values calculated from XRD assuming a C15 structure. The Debye Waller (DW) factors of the deuterides are larger than in the parent compound YFe_2 (Fig. 2b). Assuming that at 10 K the main contribution to the DW factor is due to static disorders, the increase of the DW factor is related mainly to an increase of the interatomic distance distribution.

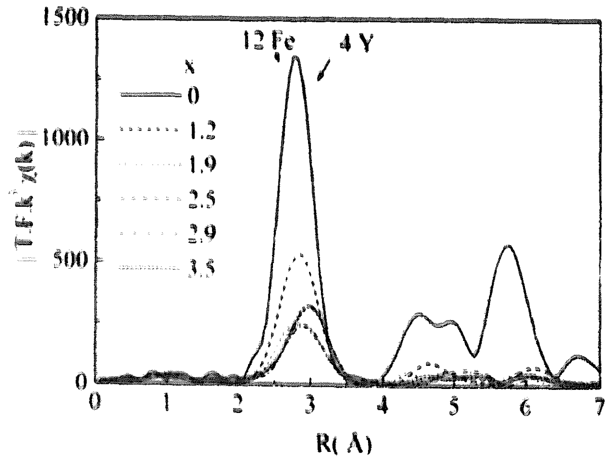

Fig. 1. Partial radial distribution function around Y atoms of YFe_2D_x compounds at 10 K.

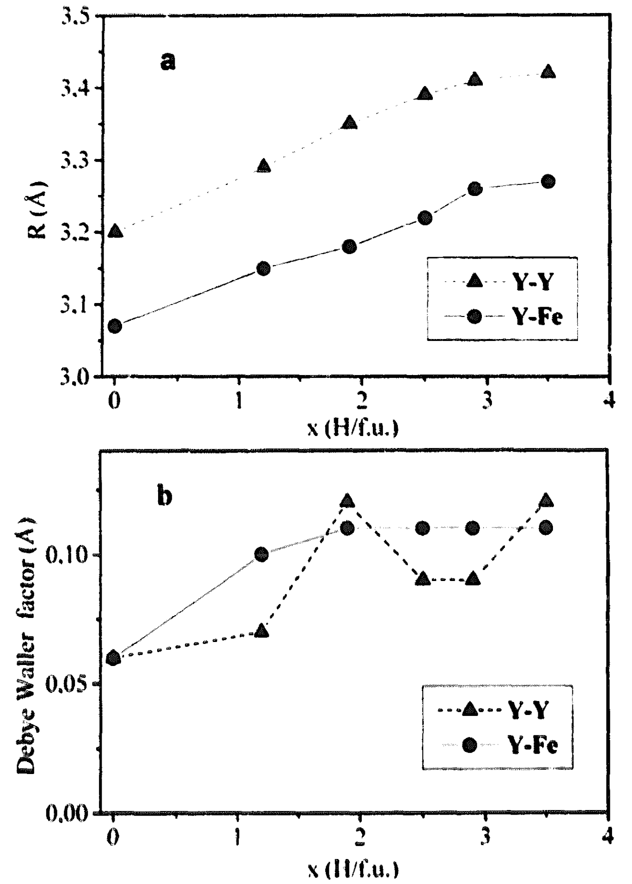

Fig. 2. Simulated Y–Fe and Y–Y interatomic distances (a) and Debye Waller factors (b) as a function of deuterium content.

At the Fe–K edge (Fig. 3) the RDF of YFe_2 shows a double peak structure corresponding to the first Fe and Y shells which are too close to be separated. Increasing deuterium content leads to a decrease of the intensity but also for $x = 1.2$, 1.9 and 2.5 to a clearer splitting of the peaks. For $x = 2.9$ and 3.5 this splitting is reduced. For all compounds the two main peaks were filtered between 1.9 and 3.4 Å and back-Fourier transformed. In the C15 structure each Fe atom is surrounded by six Fe atoms and six Y atoms. The YFe_2 EXAFS spectra can be correctly simulated considering this distance distribution, but this is no longer possible for the deuterides because a large distribution of Fe–Fe distances has to be considered. For $YFe_2D_{1.2}$ at least three different Fe–Fe distances are necessary to fit the EXAFS spectra (2 Fe at 2.45 Å, 2 Fe at 2.62 Å and 2 Fe at 2.96 Å). This is in agreement with the distance distribution calculated from the tetragonal structure with the Fe–Fe distances ranging from 2.4 to 3 Å. The first distance at 2.45 Å is smaller than that of the parent intermetallic (2.60 Å) but close to the smallest Fe–Fe distance in α-Fe (2.48 Å). It is also noteworthy that the mean value of these three distances (2.68 Å) corresponds to

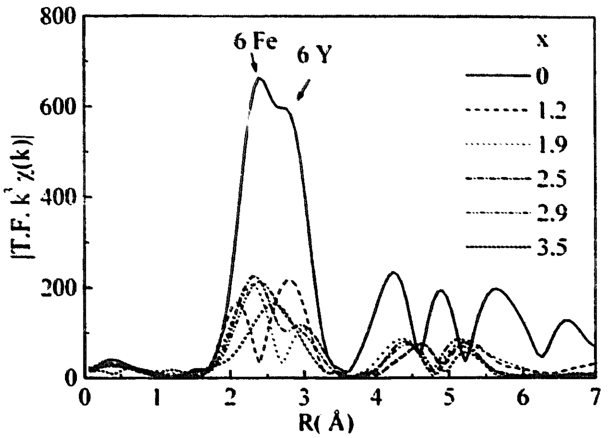

Fig. 3. Partial radial distribution function around Fe atoms of YFe_2D_x compounds at 10 K.

the average Fe–Fe distance calculated in the C15 structure. As the deuterium content increases the distribution of Fe–Fe distances becomes narrower and the average Fe–Fe value increases in agreement with the enlargement of the cell volume. For the Y shell only one distance with a large DW factor has to be considered in agreement with the Y–Fe values refined at the Y edge.

3.2. *Mössbauer spectroscopy*

The ^{57}Fe Mössbauer spectra of the YFe_2D_x compounds were collected at 4.2 K for $x = 0$, 1, 1.2, 1.9, 2.5, 2.7 and 3.5 (Fig. 4). The YFe_2 spectra are fitted with two sextets with the relative intensity ratio 3:1 according to an easy axis of magnetization along the 111 axis. For $YFe_2D_{1.2}$, five sextets with equal intensity were used to fit the spectra in agreement with the five iron sites of the crystal structure [3,4]. The sextets form two groups with a ratio 3:2 exhibiting two values for the hyperfine field (24.1 T and 19.9 T). The values for isomer shift and quadrupole splitting, however, vary significantly for all the subsextets indicating that the chemical environment is different for each of the five sublattice sites. For the other deuterides, six different sextets were used to fit the spectra, which showed some line broadening as the deuterium content increased. The spectra analysis yielded a progressive increase of the mean isomer shift which can be related to both a decrease of the s density at the ^{57}Fe nuclei and to an expansion of the lattice. Furthermore, the mean hyperfine field increases, reflecting the rise of the mean magnetic Fe moment along with D content.

4. Discussion

For all the deuterides, the Mössbauer results indicate that at least five or six different iron sites should be taken into account. This is in agreement with the large Fe–Fe distance distribution observed by EXAFS. For YFe_2D_x compounds with $x = 1.2$, 1.9 and 3.5 this Fe site distribution can be explained by the structure deviation from the C15 structure. But for $x = 2.5$ and 2.9, since the related XRD patterns can be fully indexed in the C15 structure, we may assume that either the local distortions are averaged at long range order or they are too small to be evidenced from simple powder X-ray diffraction data. The broadening of the Mössbauer lines compared to that with $x = 1.2$ and 1.9 is an indication of a more inhomogeneous distribution of Fe sites and could explain an averaging of the distortion. But the EXAFS data at the Fe edge also show that the Fe–Fe distance distribution becomes narrower and therefore the distortion should be smaller. Since it is difficult to choose between these two explanations we can also expect a combination of the two effects: weaker and less ordered structural distortions.

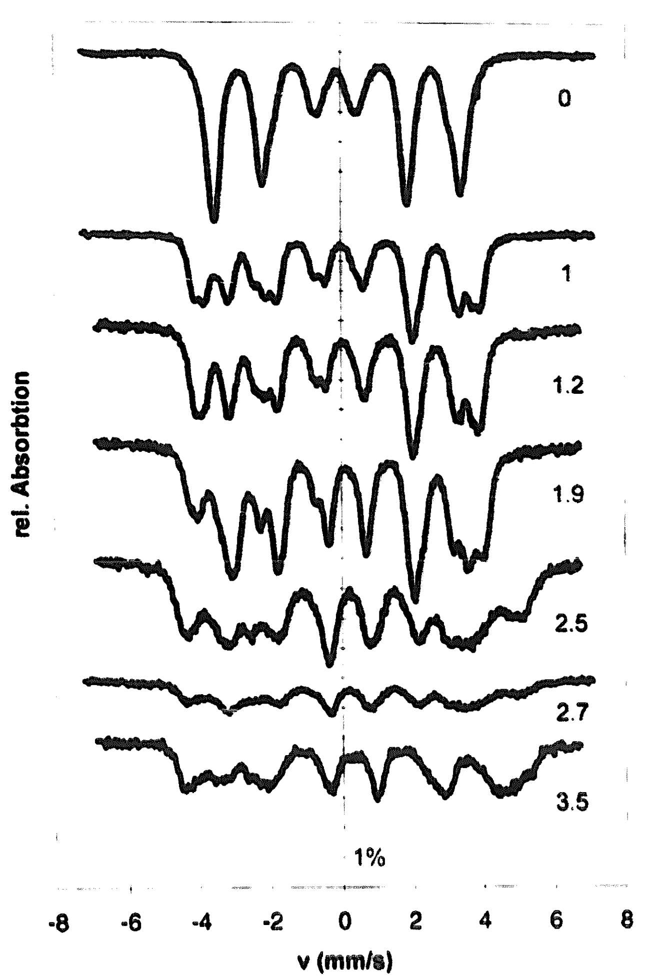

Fig. 4. ^{57}Fe Mössbauer spectra recorded from YFe_2D_x compounds at 4.2 K.

The increase of the mean Fe hyperfine field with deuterium content is in agreement with the enlargement of the total magnetic moment observed at 4.2 K. This variation can be related to the extension of the cell volume with deuterium content, which leads to an increase of the mean Fe–Fe interatomic distances. In addition, in-situ neutron diffraction experiments have shown that for $x = 1.2$, 1.9 and 3.5 the structural distortions disappear above a critical temperature which are 460, 444 and 350 K, respectively [4]. For $YFe_2D_{3.5}$ this structural transition is clearly related to Curie temperature [8]. The same behaviour is therefore expected for intermediate hydrides. The rhombohedral distortions have also been observed for other RFe_2H_x hydrides (R = Tb, Er) with H content larger than 2.4 or 3.2 H/f.u., respectively [9] and for RFe_2 compounds (R = Sm, Tb, Er and Tm) below their Curie temperatures [10]. For the intermetallics these distortions were attributed to large magnetostrictive effects. Although no structural distortion is observed for YFe_2 below its Curie temperature, it is clear that insertion of deuterium (or hydrogen) favors such magnetostrictive effects. In addition, EXAFS results have shown the existence of very short Fe–Fe distances for the deuterides, whereas the Fe–Y and Y–Y distances are comparable to those expected from the C15 structure. Since in YFe_2D_x compounds only the Fe atoms are magnetic, this behaviour can be explained by stronger Fe–Fe interactions. But due to the lowering of the crystal symmetry deuterium ordering in some preferential interstitial sites can also be expected which will enhance the Fe site distribution.

5. Conclusion

In this work the local order of the YFe_2D_x deuterides was characterized by EXAFS and ^{57}Fe Mössbauer spectroscopy indicating a large distribution of Fe sites and Fe distances. For $x = 1.2$, 1.9 and 3.5 this can be explained by the structural distortions observed by XRD, whereas for $x = 2.5$ and 2.9 these local distortions should be small or averaged since they are not observed by XRD. In relation to neutron diffraction, these distortions should result from strong magnetic interactions between Fe atoms.

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