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Influence of deuterium absorption on structural and magnetic properties of $ErFe_2$

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Abstract

The structural and magnetic properties of $ErFe_2D_x$ deuterides ($1.3 \leq x \leq 3.5$) were investigated by X-ray diffraction, magnetization measurements, Mössbauer spectroscopy and X-ray magnetic circular dichroism (XMCD). While structural studies revealed the maintenance of the C-15 structure for $x<3$, ^{57}Fe Mössbauer spectroscopy indicates the formation of several different local environments of the Fe-sites upon deuterium absorption. Further deuterium absorption ($3.4 \leq x \leq 3.6$) led to a rhombohedral distortion and to a decrease of the local Fe and Er moments. The XMCD spectra of $ErFe_2D_{3.4}$ at the Fe-K edge display a complex behaviour versus temperature, which is attributed to the great influence of the Er neighbours below the compensation temperature. In addition the XMCD signal collapses at both the Er-L_{III} edge and Fe-K edge when crossing the compensation point.

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

1. Introduction

The influence of hydrogen absorption on the thermodynamic, structural and magnetic properties of RM_2 (R= rare earth, M=transition metal) Laves phase compounds has been widely studied for several decades [1,2]. The RFe_2 compounds are of particular interest due to their ability to form several RFe_2H_x hydrides with concentrations ranging from 1.2 to 5 H/f.u. [3–5]. In YFe_2 hydrogen (deuterium) absorption induces the formation of hydrides (deuterides) with at least seven different structures derived from the C15 structure of the parent intermetallic due to H (D) order in interstitial sites accompanied by a displacement of the metallic atoms [6]. $ErFe_2$ hydrides have also been studied in detail by several groups [4,7,8]. From neutron diffraction studies on $ErFe_2D_x$ ($x \leq 3.5$) deuterides a collinear ferrimagnetic structure was derived [4,8]. However K. Shashikala et al. [9] have interpreted the reduction of the ordered moments upon H absorption by a non-collinear orientation of the Fe moments rather than by a fanning of the Er moments. In order to understand more clearly the influence of the deuterium on the structural and local magnetic properties of the $ErFe_2$ we have performed X-ray diffraction, magnetization, ^{57}Fe Mössbauer spectroscopy and X-ray magnetic circular dichroism (XMCD) studies. These results will be discussed in relation to the structural and magnetic properties of YFe_2D_x deuterides.

2. Experimental

$ErFe_2$ intermetallic compound was prepared and characterized as in Ref. [3]. The $ErFe_2D_x$ deuterides were synthesized by deuterium absorption at 408 K for $1.3 \leq x \leq 2.5$ and at 300 K for $x=3.4$ using a Sievert method. They were characterized by X-ray diffraction (XRD) at 300 K with a D8 Bruker diffractometer (Cu Kα radiation). The magnetic measurements were performed for $B_{ext}<1.8$ T between 4.2 and 500 K with a DSM8 Manics magnetosusceptometer and for $B_{ext}<6$ T between 5 and 290 K with a SQUID quantum-design magnetometer. The ^{57}Fe Mössbauer spectra were recorded between 4.2 K and 300 K using a conventional constant acceleration type spec-

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trometer. The data were analyzed as described in Ref. [5]. The XMCD measurements have been performed at the Fe-K edge and at the Er-L_3 edges on the D11 spectrometer on the DCI ring at LURE (Orsay). The external applied field was 1.8 T and the temperature ranged between 10 and 300 K. The experimental details are given in [10,11]. All the XMCD spectra were calibrated with a Fe or Ni metal foil and normalized to the height of the absorption edge.

3. Results and discussion

3.1. X-ray diffraction

The XRD patterns of the $ErFe_2D_x$ deuterides with $1.3 \leq x \leq 2.5$ were all refined in the cubic C15 structure ($Fd\bar{3}m$ space group) without any visible distortion or superstructure lines. This reveals a different structural behaviour from YFe_2D_x with similar D content [3]. For $x = 3.5$ the pattern was refined in a rhombohedral structure ($R\bar{3}m$ space group). The lattice parameters are given in Table 1.

3.2. Magnetization measurements

The thermomagnetic measurements show in agreement with previous results [4] that the compensation temperature ($T_{comp.}$) decreases as the deuterium content increases, due to a weakening of the Er–Fe interaction. T_{comp} decreases linearly with the cell volume from $x = 0$ to 2.5. Then a discontinuity is observed between the cubic and the rhombohedral ($x = 3.5$) deuterides. The Curie temperature for the deuterides with $1.3 \leq x \leq 2.5$ could not be measured due to deuterium desorption at high temperature. For $x = 3.5$, T_c is near 300 K. The magnetization of all the deuterides measured at 4.2 K shows a large hysteresis effect between the first magnetization curve and the second one, the width of the hysteresis increasing with the amount of deuterium (Fig. 1). Since RFe_2 compounds exhibit substantial low temperature anisotropy, this might be attributed to the formation of pinning centers in the deuterides. The larger the amount of hydrogen in the sample the more difficult it is to gain magnetic saturation, a situation which is commonly observed in RFe_2 hydrides and is attributed to the fanning of the magnetic moments.

Table 1
Lattice parameters of the $ErFe_2D_x$ samples (a, c): Mean values of isomer shift $\langle \delta \rangle$ (relative to the source) and magnetic hyperfine field $\langle B_{eff} \rangle$ at 4.2 K obtained from the computer fit described in the text

Samples	a, c (Å)	$\langle \delta \rangle$ [mm/s]	$\langle B_{eff} \rangle$ [T]
$ErFe_2$	7.283	−0.08	21.83
$ErFe_2D_{1.3}$	7.555	−0.17	22.11
$ErFe_2D_{1.9}$	7.612	0.09	21.54
$ErFe_2D_{2.5}$	7.665		
$ErFe_2D_{3.5}$	5.579, 13.233	0.31	18.36

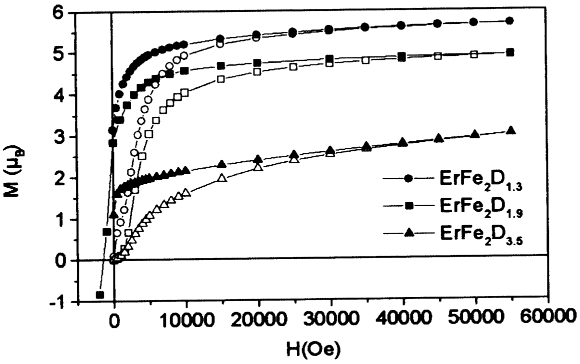

Fig. 1. Magnetization curves of $ErFe_2D_x$ samples ($x = 1.3$, 1.9 and 3.5) at 4.2 K. The open symbols correspond to the first magnetization curve and the filled symbols to the second magnetization.

3.3. Mössbauer spectroscopy

Although in the C15 structure all Fe-sites are crystallographically equivalent, the ^{57}Fe Mössbauer spectrum of $ErFe_2$ consists of two sextets with the intensity ratio of 3:1 (Fig. 2). This is due to different contributions to both quadrupole interaction and hyperfine field for the Fe-sites, depending upon the angle between the main axis of the electric field gradient (EFG) and the ^{57}Fe hyperfine field (antiparallel to the Fe moment) when the easy axis of magnetization deviates from [0,0,1]. In $ErFe_2$ the easy axis of magnetization is [1,1,1] and adds to the two contributions with a ratio of 3:1. Despite the fact that the C15

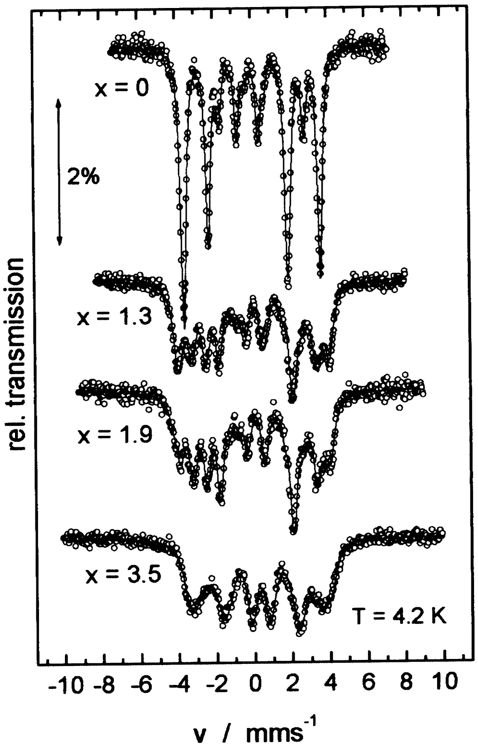

Fig. 2. Experimental data at 4.2 K (○) and calculated (–) ^{57}Fe Mössbauer spectra of $ErFe_2$, $ErFe_2D_{1.3}$, $ErFe_2D_{1.9}$ and $ErFe_2D_{3.5}$.

structure is maintained for $1.3 \leq x \leq 2.9$, the spectra recorded from $ErFe_2D_x$ exhibit a complex shape, even for the lowest deuterium concentration ($x = 1.3$). The hyperfine interactions are of an extremely short range order and may evidence fluctuations in the local environment which are below the resolution of an X-ray experiment. It was not possible to refine correctly the experimental data with several sextets of equal intensity. A possible assumption is that [1,1,1] remains the easy axis of magnetization and that two types of local environments with equal magnitude, significantly different from each other, exist. Indeed, a reasonable fit was obtained assuming the presence of four sextets with the intensity ratio of 3:1:3:1 (Fig. 2) even in the case of $ErFe_2D_{1.9}$, where the situation is more complex. However the distinct change of the spectra shape of $ErFe_2D_{1.9}$ compared to $ErFe_2D_{1.3}$, indicates that the number of inequivalent Fe sites has increased further. The pattern asymmetric shape indicates a variety of EFG and isomer shift values which has to be attributed to several different local environments of the Mössbauer nuclei, each characterized by its own local symmetry and chemical environment. For $x = 3.5$ the magnetically split spectra broadens, and tends to a more symmetric shape. Since the T_C of $ErFe_2D_{3.5}$ is already below room temperature, the spectrum at 300 K consists merely of a superposition of quadrupole split doublets (Fig. 3). After several attempts a fit using five doublets with the intensity ratio 1:1.2:1.4:1.6:1.8 was performed (Fig. 3), thereby relating isomer shift and quadrupole values ($\Delta\delta = +0.05$ mm/s per spectrum and $\Delta = +0.015$ mm/s per spectrum). Using the same intensity ratio the spectrum at 4.2 K was analyzed (Fig. 2). A reasonable fit was obtained but since the isomer shift values were found to be essentially constant, the assumption made above has to be modified. As in the case of YFe_2D_x [5] this should indicate that the insertion of D atoms in the RFe_2 lattice induces not only a volume expansion but also a local distortion due to a displacement of the Fe atoms, even if this is not observed at long range order by XRD or neutron diffraction. This also means that the Fe sites are not all equivalent and may have various D atom environments, which will influence their local magnetic properties. The mean values of the isomer shift $<\delta>$ (Table 1) increase continuously as expected from the cell volume increase. The mean magnetic hyperfine field $\langle B_{eff} \rangle$ (Table 1) increases slightly then decreases upon further deuterium absorption. For $x = 4.1$ the Mössbauer spectra shows only a doublet at 4.2 K [12] indicating a large magnetization decrease. This behaviour may be explained by the filling of the conduction band by D electrons, leading to a transition from a strong ferromagnetic to a weak ferromagnetic state for Fe moments. In YFe_2D_x the transition from a strong to a weak magnetic state occurs for $x = 4.2$ through a metamagnetic transition around 90 K [13].

3.4. X-ray magnetism circular dichroism

The normalized XMCD signal at the Fe-K edge for $x = 0$, 1.9, 2.5 and 3.5 at 11 K are presented in Fig. 4a. The XMCD signal at the Fe-K edge has been depicted as the sum of three contributions: one purely atomic (the Fano effect), one called local due to the spin polarization of the p-state of the absorbing site and the last one due to the

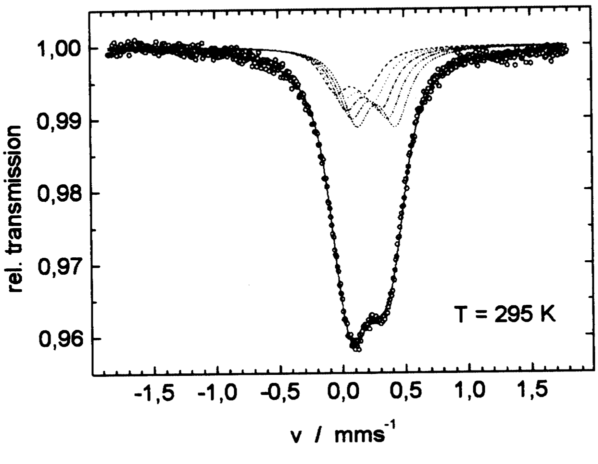

Fig. 3. Experimental (○) and calculated (–) ^{57}Fe Mössbauer spectra of $ErFe_2D_{3.5}$ at 295 K. The dotted curves correspond to the five doublets necessary to refine the spectra.

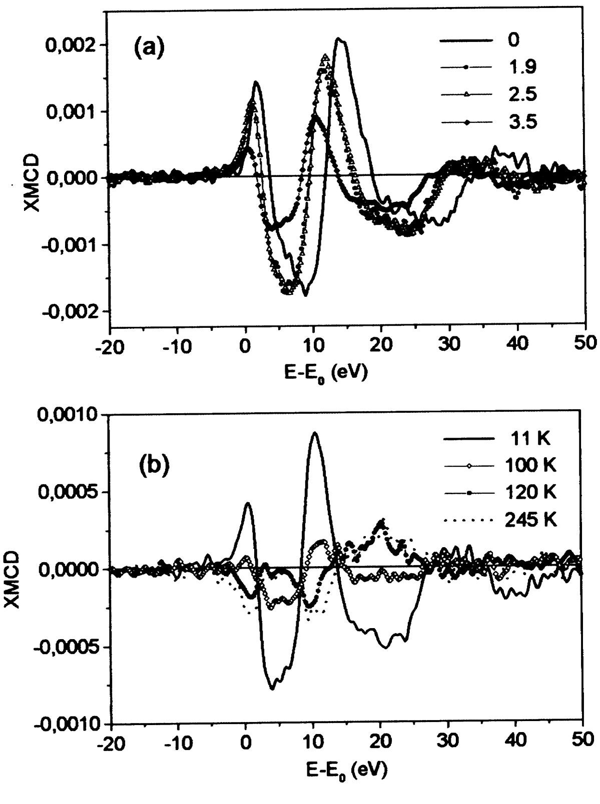

Fig. 4. Normalized XMCD spectra at the Fe-K edge: (a) for $ErFe_2$, $ErFe_2D_{1.9}$, $ErFe_2D_{2.5}$ and $ErFe_2D_{3.5}$ at 11 K (the curve labels correspond to the D content), (b) for $ErFe_2D_{3.5}$ at different temperatures.

spin–orbit scattering of the photoelectron by the neighbours and the absorber [14]. The shape of the signal is similar for all the compounds, but we observe a decrease of the intensity and a shift of the peak towards lower energy as the D content increases. Compared to Fe metal [10] the intensity of the peak around 6 eV is greater and a large additional contribution is observed at 12 eV (10 eV for $x=3.5$). This structure which is not observed in the Fe XMCD signal of $LuFe_2$ but visible in $ErFe_2$ should be related to the coupling with the Er 4f spin contribution which is dominant at low temperature. As the temperature increases (Fig. 4b) the intensity of the peaks in the XMCD of $ErFe_2D_{3.5}$ decreases, crossing zero at the compensation temperature which is near 100 K for this composition. Above this temperature the sign of the peaks is inversed, due to the reorientation of the Fe moments parallel to the applied field. However it is noticeable that the large peak centred at 5 eV is no longer visible above T_{comp}. The multiple scattering calculations performed at the Co K edge by Rueff [15] on $TbCo_2$, isostructural to $ErFe_2$, shows the dominant contribution of the scattering of the photoelectron by the Tb neighbours on the dichroic signal compared to the characteristic of the Co metal. A further analysis shows that this contribution is mainly due to the d states of the Tb atoms. Due to the similarities of the dichroic signal at the Co K edge in $TbCo_2$ and at the Fe K edge in $ErFe_2$, it can be assumed that the influence of the Er-d spin contribution should dominate below the compensation temperature. Above T_{comp} the Fe magnetization becomes dominant and the signal due to the Er d states is reduced, leading to a modification of the dichroic signal shape. Similar multiple scattering calculations will be undertaken at the Fe-K edge on $ErFe_2$ in order to elucidate the behaviour of $ErFe_2D_{3.5}$ versus temperature.

The normalized XMCD data at the Er L_{III} edge and 11 K for $ErFe_2D_x$ with $x=1.9$, 2.5 and 3.5 are depicted in Fig. 5a. In all cases the signal is like for $ErFe_2$ [16] built up from two peaks which can be attributed to the 4f electric quadrupolar transition (first peak) and the 5d electric dipolar transition (second peak). The sign of the 4f contribution is in agreement with what is expected from calculations, whereas the sign of the 5d contribution, which should be parallel to the 4f, is opposite to the expected direction. This was explained by the spin dependence of the radial part of the matrix element on the spin of the electrons [17–19]. Like at the Fe-K edge, the XMCD signal of $ErFe_2D_{3.5}$ is smaller and shifted to lower energy compared to the two cubic deuterides. The decrease of the peak intensity indicates a lowering of the Er moment. The shift of the peak towards lower energies needs further studies and should be related to the modification of the DOS and to the shift of the Fermi level. The evolution of the XMCD signal in $ErFe_2D_{3.5}$ versus temperature (Fig. 5b) shows that the peak intensities decrease until almost zero at the $T_{comp.}$ and increase again with a change of sign above this temperature. The integrated intensity of the peak follows the temperature variation of the magnetization. The disappearance of the signal at $T_{comp.}$, where both the Er and Fe moments are of equal magnitude, may be explained by a random distribution of domains where the Er (Fe) moments are parallel or antiparallel to the applied field. There is probably not enough magnetic energy to orientate the moments along one preferred direction.

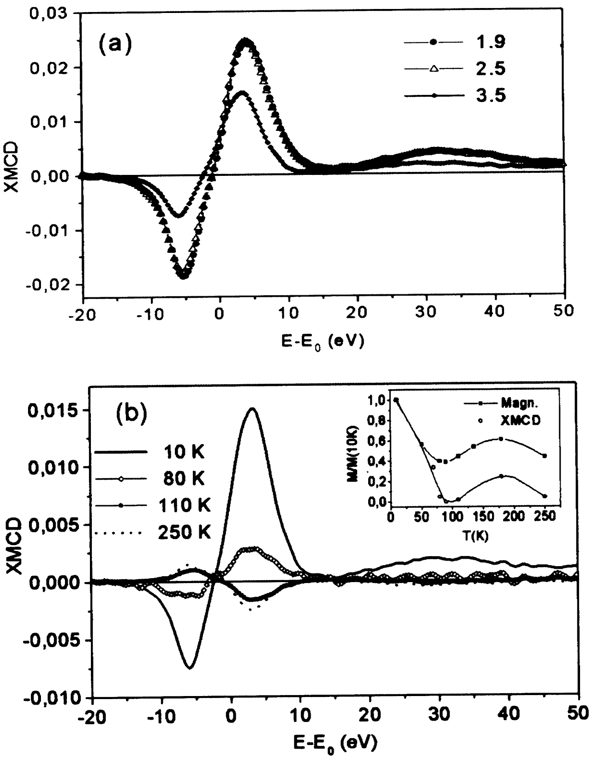

Fig. 5. Normalized XMCD spectra at the Er-L_{III} edge: (a) for $ErFe_2D_{1.9}$, $ErFe_2D_{2.5}$ and $ErFe_2D_{3.5}$ at 11 K (the curve labels correspond to the D content), (b) for $ErFe_2D_{3.5}$ at different temperatures.

4. Conclusion

The analysis of the $ErFe_2D_x$ XRD patterns for $1.3 \leq x \leq 2.5$ did not reveal any structural distortion or superstructure lines contrary to the YFe_2 deuterides [3]. Since the metallic radius of Er is smaller than that of Y, the structural instability in the C15 structure, related to the ratio between the rare earth and transition metal radius, is lower in $ErFe_2$ than in YFe_2 which may prevent an ordered displacement of the metallic atoms upon H absorption. Nevertheless, the Mössbauer study shows that a local distribution of the Fe sites still exists like in the YFe_2 deuterides [6]. The reduction of the magnetization of $ErFe_2D_{3.5}$ at 4.2 K compared to the deuterides with lower deuterium content is related to a reduction of the Fe and Er moments as observed by Mössbauer spectroscopy and XMCD. This reduction may result from the additional electrons supplied by deuterium which enter the minority conduction band. The XMCD study on $ErFe_2D_{3.5}$ shows a complex behaviour at the Fe-K which is attributed to the strong influence of the Er neighbours' contribution on the shape of the signal.

References

[1] K. Yvon, P. Fischer, in: L. Schlapbach (Ed.), Hydrogen in Intermetallic Compounds I, Topics in Applied Physics, Vol. 63, Springer Verlag, Berlin–Heidelberg, 1988.
[2] Y. Fukai, The Metal–Hydrogen System, Springer Verlag, Berlin, 1993.
[3] V. Paul-Boncour, L. Guénée, M. Latroche, A. Percheron-Guégan, B. Ouladdiaf, F. Bourée-Vigneron, J. Solid State Chem. 142 (1999) 120.
[4] D. Fruchart, Y. Berthier, T. de Saxce, P. Vuillet, J. Less-Common Met. 130 (1987) 89.
[5] V. Paul-Boncour, S.M. Filipek, A. Percheron-Guégan, I. Marchuk, J. Pielaszek, J. Alloys Comp. 317–318 (2001) 83.
[6] V. Paul-Boncour, G. Wiesinger, Ch. Reichl, M. Latroche, A. Percheron-Guégan, R. Cortes, Physica B 307 (2001) 277.
[7] A.V. Deryagin, N.V. Kudrevatykh, V.N. Moskalev, N.V. Mushnikov, Phys. Met. Metall. 38 (1984) 96.
[8] J.J. Rhyne, G.E. Fish, S.G. Sankar, W.E. Wallace, J. Physique 40 (1979) C5–209.
[9] K. Shashikala, P. Raj, A. Sathyamoorthy, T.V. Chandrasekhar Rao, V. Siruguri, S.K. Paranjpe, Phil. Mag. B 79 (1999) 1195.
[10] F. Baudelet, Ch. Brouder, E. Dartyge, A. Fontaine, J.P. Kappler, G. Krill, Europhys. Lett. 13 (1990) 751.
[11] F. Baudelet, E. Dartyge, A. Fontaine, Ch. Brouder, G. Krill, J.P. Kappler, M. Piecuch, Phys. Rev. B 43 (1991) 5857.
[12] B.D. Dunlap, G.K. Shenoy, J.M. Friedt, P.J. Viccario, D. Niarchos, H.A. Kierstead, A.T. Aldred, D.G. Westlake, J. Appl. Phys. 50 (1979) 7682.
[13] V. Paul-Boncour, A. Percheron-Guégan, J. Alloys Comp. 293–295 (1999) 237.
[14] Ch. Brouder, M. Alouani, K.H. Bennemann, Phys. Rev. B. 54 (1996) 7334.
[15] J.-P. Rueff, PhD Thesis, University Joseph Fourier, Grenoble, 1997.
[16] Ch. Giorgetti, E. Dartyge, F. Baudelet, Ch. Brouder, Appl. Phys. A 73 (2001) 703.
[17] J.C. Lang, S.W. Kycia, X.D. Wang, B.N. Harmon, A.I. Goldman, D.J. Branagan, R.W. McCallum, K.D. Finkelstein, Phys. Rev. B 46 (1992) 5298.
[18] X.D. Wang, T.C. Leung, B.N. Harmon, P. Carra, Phys. Rev. B 47 (1993) 9087.
[19] P. Carra, B.N. Harmon, B.T. Thole, M. Altarelli, G.A. Sawatsky, Phys. Rev. Lett. 66 (1991) 2495.