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Neutron diffraction study of ZrM_2D_x deuterides (M=Fe, Co)

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Abstract

The structure of $ZrFe_2$ and $ZrCo_2$ deuterides prepared under very high deuterium pressure has been studied by neutron diffraction (ND) at 10 K. The patterns of both compounds are refined with a mixture of intermetallic compound and deuteride. For $ZrFe_2D_x$, the cell volume increases with 23% and the 2.7 D/f.u. are located randomly in A2B2 sites. The Fe moments order in a ferromagnetic structure and increase from 1.8 to 2.2 μ_B/Fe upon D absorption. The $ZrCo_2$ deuteride shows a doubling of the cell parameter due to deuterium order of 2 D/f.u. in 7 over 12 A2B2 sites with a cell volume increase of 12%.

Keywords: Hydrogen storage materials; Gas–solid reactions; Neutron diffraction; Neutron scattering; Magnetic measurements

1. Introduction

During recent decades, hydrogen absorption and its influence on structural, magnetic and electronic properties of Laves phase compounds were intensively studied [1–3]. Large numbers of these compounds, especially those in which the rare earth element is one of their components, have a high hydrogen absorption capacity even at pressures lower than 1 MPa. However, in systems like $ZrFe_2$ and $ZrCo_2$ the amount of absorbed hydrogen was found to be limited to 0.35 D/f.u. for pressures up to 7 MPa [4]. The application of high hydrogen or deuterium pressure ($P=$ 0.7 GPa) allowed us to form hydrides or deuterides of $ZrFe_2$ and $ZrCo_2$ [5]. X-ray diffraction analysis showed that these two hydrides retain the C15 type cubic structure with, respectively, 8 and 4.5% of lattice parameter increase. In order to clarify the H sites occupancy, neutron diffraction experiments have been performed at 10 K on the corresponding ZrM_2D_x deuterides.

2. Experimental

The samples were prepared by arc melting of the appropriate amount of metals under argon atmosphere. The quality of the samples was checked by XRD and microprobe analysis. Samples were located in the high pressure apparatus described elsewhere [6] and treated at 100 °C in vacuum before hydrogen charging. The hydrogenation was usually performed at pressures up to 0.7 GPa and temperatures up to 100 °C during 2 to 5 days. In order to avoid possible hydrogen desorption the apparatus was cooled down to −60 °C, then the pressure was reduced to atmospheric value and the samples were immediately transferred in liquid nitrogen.

The X-ray diffraction (XRD) measurements were performed at room temperature using a D8 Brucker diffractometer between 10° and 120° in 2θ and a step of 0.02° (Cu Kα wavelength).

The neutron diffraction (ND) experiments were performed on the high resolution 3T2 spectrometer located at the LLB (Saclay, France). The wavelength was 1.225 Å. The patterns were registered at 10 K, to avoid deuterium desorption during the time of the experiment, which was about 24 h for each spectrum. The samples were trans-

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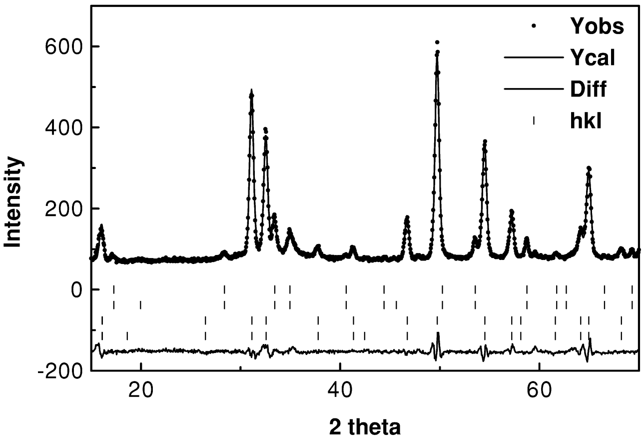

Fig. 1. Neutron diffraction pattern of $ZrFe_2D_x$ refined with a mixture of $ZrFe_2$ and $ZrFe_2D_{2.7}$ with both nuclear and magnetic contributions (see Table 1).

ferred from vessels kept in liquid nitrogen to vanadium tubes adapted for the neutron experiments and then introduced in the cryostat already cooled at 100 K. The time of transfer was below 15 min. The XRD and ND patterns were refined with the FULLPROF code [7].

The magnetic measurements were performed on a DSM8 magneto-susceptometer with applied fields up to 1.6 T. The magnetisation was measured as a function of temperature (from 4.2 to 300 K) with an applied field of 1 T. Measurements at temperatures higher than 300 K were not available due to the fast deuterium desorption from the sample above room temperature.

3. Results and discussion

3.1. $ZrFe_2D_x$

Both the XRD and ND patterns show a mixture of $ZrFe_2$ and $ZrFe_2D_x$ indicating that despite all the care to store and transport the samples it was not possible to avoid partial deuterium desorption. However this means that we are on the plateau and that the deuteride contribution corresponds to the phase β_{min} with a minimum D content. The cell parameters measured at 300 K by XRD are 7.070(1) Å for $ZrFe_2$ and 7.567(1) for $ZrFe_2D_x$ whereas at 10 K by ND they are 7.061(1) Å for $ZrFe_2$ and 7.562(1) for $ZrFe_2D_x$. The weak decrease of the cell parameters from 300 to 10 K is, within the experimental errors, due to the thermal contraction. The refined neutron diffraction pattern of $ZrFe_2D_x$ at 10 K is presented in Fig. 1. The results of the refinement are given in Table 1: both phases crystallize in the cubic C15 structure described in the $Fd\bar{3}m$ space group. The Rietveld analysis leads to 12% of $ZrFe_2$ and 88% of deuteride. The deuterium atoms in $ZrFe_2D_x$ are located in the 96*g* A2B2 site with an occupancy factor corresponding to 2.7 D/f.u., which is lower than the value of 3.5 D/f.u. estimated from the cell volume increase ($\Delta V = 80.72$ Å^3) and assuming a volume expansion of 2.85 Å^3/D atom as it was estimated from other ZrM_2 compounds (M=V, Zr and Mn) [5]. The occupation of the A2B2 sites is in agreement with the predictions of a simple binary hydrides model [8]. In

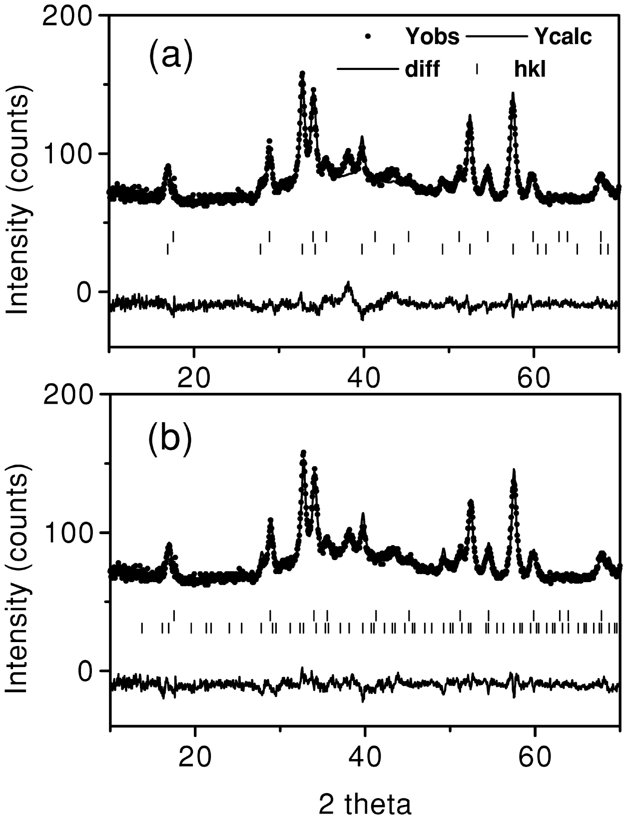

Fig. 2. Neutron diffraction pattern of $ZrCo_2D_x$ with a mixture of $ZrCo_2$ (cubic C15) and $ZrCo_2D_2$ refined with (a) a cubic C15 structure with parameters of Table 2 and (b) a cubic superstructure with a doubling of the cell parameter and parameters of Table 3.

Table 1
Results of the refinement of $ZrFe_2D_x$ at 10 K with the $ZrFe_2$ and $ZrFe_2D_n$ phases described in the $Fd\bar{3}m$ space group

Phase	*a* (Å)	*V* (Å^3)	% Phase	M/$_{Fe}$ (μ_B)	R_B (%)	R_{mag} (%)
$ZrFe_2$	7.061(1)	352	12	1.8	9.90	8.23
$ZrFe_2D_n$	7.562 (1)	432.8	88	2.2	5.72	5.68
	$\Delta a/a = 7.1\%$	$\Delta V/V = 22.9\%$				
D_{A2B2} 96*g*		$x = 0.3147$	$z = 0.1294$		$N = 0.222$	
Total D/f.u.					2.66 (2)	

agreement with previous magnetic measurements, the Fe moments order in a ferromagnetic structure with an increase of the magnetization compared to the parent intermetallic compound. The Fe moment in the deuteride is close to that of pure b.c.c. Fe (2.22 μ_B). Since the saturation magnetization of the deuteride at 4.2 K was only 1.88 μ_B/Fe, the difference should be attributed to an induced moment of -0.70 μ_B induced on the Zr site and close to the -0.56 μ_B found by Dumelow et al. [9] from the pressure dependence of the hyperfine field of $ZrFe_2$.

3.2. $ZrCo_2D_x$

Like $ZrFe_2D_x$ a mixture of $ZrCo_2$ and $ZrCo_2D_x$ is observed in the XRD and ND patterns. The ND pattern was refined assuming that $ZrCo_2D_x$ crystallizes in the C15 type structure with D atoms in A2B2 sites. The refined pattern is presented in Fig. 2 and the results of the analysis in Table 2. The amount of $ZrCo_2$ represents about 1/3 of the sample, which is related to the fact that the $ZrCo_2$ deuteride is less stable than $ZrFe_2$ [5]. The cell volume increase is 11.6% and the total amount of D atom in the 96*g* A2B2 site is 1.65 D/f.u. close to the calculated value of 1.72 D/f.u. Considering the refinement of the ND pattern in Fig. 2, one can notice that the lines are very broad and their intensity weak. The large bump centred around 35° (2 Å) should be attributed either due to a partial amorphization of the sample or to a short range order correlation between D atoms. In addition there is an additional reflection at 38° ($d = 1.87$ Å) and the intensity of the lines at 35° and 43.2° are not correctly refined. These lines could not be attributed to products of decomposition like zirconium deuterides or cobalt and were also not observed in the corresponding XRD pattern. It is possible to take into account these additional lines by doubling the cubic cell parameter. This superstructure can be described in the $F\bar{4}3m$ space group, with five Zr sites, four Co sites and 12 possible A2B2 sites. Since no superstructure lines were observed in the XRD pattern, the atomic positions of the Zr and Co atoms were fixed to those derived from the C15 structure. The positions and occupancy factors of the D atoms were refined (Table 3), and only seven sites were found partially occupied leading to a total number of 2 D/f.u. This value is larger than the one calculated in the C15 structure, due to the additional intensity of the line at 38°. This result and the one obtained for $ZrFe_2$ deuteride

Table 2
Results of the refinement of $ZrCo_2D_x$ at 10 K with the two phases described in the $Fd\bar{3}m$ space group

Phase	S.G.	a (Å)	V (Å^3)	% Phase	R_B
$ZrCo_2$	$Fd\bar{3}m$	6.933(1)	333.25	33.4	10.9
$ZrCo_2D_n$	$Fd\bar{3}m$	7.191(1)	371.83	66.6	9.02
		$\Delta a/a = 3.7\%$	$\Delta V/V = 11.6\%$		
D_{A2B2} 96*g*	$x = 0.3425(1)$	$z = 0.1174(1)$	$N = 0.137(2)$	$= 1.65$ D/f.u.	
χ^2	3.02	R_p (%)	26.6		

Table 3
Results of the refinement of $ZrCo_2D_x$ at 10 K with the deuteride phase described in a superstructure with the $F\bar{4}3m$ space group

Phase	S.G.	a (Å)	V (Å^3)	% Phase	χ^2	R_B (%)
$ZrCo_2$	$Fd\bar{3}m$	6.933(1)	333.25	30	2.28	5.92
$ZrCo_2D_x$	$F\bar{4}3m$	14.385(2)	2977.03	70		10.08
		(2×7.193)	(8×372.1)			
Atoms	Site	x	y	z	N	B
Zr1	4*a*	0	0	0	1	3.825
Zr2	4*b*	0.5	0.5	0.5	1	
Zr3	24*f*	0	0.25	0.25	1	
Zr4	16*e*	0.125	0.125	0.125	1	
Zr5	16*e*	0.625	0.625	0.625	1	
Co1	16*e*	0.375	0.375	0.375	1	0.133
Co2	16*e*	0.8125	0.8125	0.8125	1	
Co3	48*h*	0.06225	0.06225	0.8125	1	
Co4	48*h*	0.06225	0.06225	0.3125	1	
D1	48*h*	0.001(4)	0.114(2)	0.114(2)	0.42(7)	1.22
D2	48*h*	0.509(6)	0.850(5)	0.350(5)	0.17(4)	
D3	48*h*	0.450(922)	0.900(100)	0.950(922)	0.062(3)	
D4	48*h*	0.148(340)	0.737(284)	0.264(284)	0.20(2)	
D5	96*i*	0.753(229)	0.849(181)	0.112(148)	0.40(2)	
D6	96*i*	0.869(168)	0.487(228)	0.233(219)	0.330(2)	
D7	96*i*	0.224(215)	0.833(294)	0.088(313)	0.198(4)	
Total D/f.u.					2.03(3)	

show that for samples prepared under very high hydrogen pressure a simple model stating that the cell volume should increase by 2.85 $Å^3$/D is not valuable. The lowering of symmetry and the existence of superstructure due to deuterium order has already been observed in other systems like in YFe_2–D_2 [10]. The magnetic measurements of $ZrCo_2$ and its deuteride show a similar behaviour for both compounds: a very weak ferromagnetism with $M_s = 0.021\ \mu_B$/f.u. and a slope $\chi = 1.7 \times 10^{-3}$ emu/mole which is nearly independent of the temperature. These values are only slightly larger than in Ref. [11] where the magnetic moment of $ZrCo_2$ at 4.2 K was estimated to be $4 \times 10^{-3}\ \mu_B$/f.u. and the susceptibility at 300 K 8×10^{-4} emu/mole.

4. Conclusions

Both $ZrFe_2$ and $ZrCo_2$ are able to absorb hydrogen or deuterium under gaseous pressure of 1 GPa. The neutron diffraction analysis performed at 10 K show that $ZrFe_2D_n$ crystallizes in a cubic C15 type structure ($a = 7.562$ Å) with 2.7 D/f.u. located randomly in A2B2 sites. This deuteride is ferromagnetic with an increase of the Fe moment to 2.2 μ_B compared to the 1.8 μ_B of the parent compound. The ND analysis of $ZrCo_2$ deuteride indicates a doubling of the cell parameter ($a' = 2a = 14.385$ Å) due to deuterium order of 2 D/f.u. in 7 among 12 A2B2 sites. The magnetic properties of $ZrCo_2D_2$ remain almost unchanged compared to those of the parent intermetallic. For both compounds prepared under high hydrogen pressure the cell volume increase is different from the 2.85 Å/H observed for other ZrM_2 hydrides.

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