Experimental report

24/02/2021

Proposal: **EASY-593** **Council:** 10/2019

Title: Solving the structure of ()TiFe0.95Mn0,05D monodeuteride by high resolution neutron diffraction

Research area: Materials

This proposal is a new proposal

Main proposer: **Michel LATROCHE**

Experimental team:

Local contacts: Laetitia LAVERSENNE

Samples: TiFe0.95Mn0.05D

Instrument	Requested days	Allocated days	From	To
D2B	2	2	19/08/2020	20/08/2020

Abstract:

TiFe(Mn) is a promising system for H2 storage with a di-hydride having a gravimetric capacity of 1.86 wt.% H2. Upon hydrogen absorption, consecutive formation of monohydride β-TiFe(Mn)H and dihydride γ-TiFe(Mn)H2 occurs. The phase transformations have been successfully characterized by in-situ neutron diffraction analysis on D1B during deuteration of the TiFe0.85Mn0,05 while recording the Pressure-Composition Isotherms (PCI) at RT between 0.1 < PD2 < 100 bar (proposal CRG 5-22-201). However, the two hydrides crystallize in orthorhombic structures with different space groups: P2221 and Cmmm for β- and γ-phases respectively. In addition, two different β-phases have been reported, with composition and occurrence depending on sample history. For all these structures, hydrogen atoms are located in octahedral sites.

The D1B experiment allowed to characterize the phase transitions but not to fully solved the structure of the β-monohydride due to low resolution of D1B at high angles. Therefore, acquisition of high-resolution data for this mono-hydride will be mandatory to fully solve its structure and to completely analyse the in-situ neutron diffraction data collected on D1B.

31/01/2021

Experimental Report

Proposal: EASY-593 **Council: 2020**

Title: Solving the structure of gamma-TiFe0.85Mn0,05D2 deuteride by high resolution neutron diffraction

This proposal is a new proposal
Research Area: Chemisty

Main proposer: LATROCHE Michel

Experimental Team: CUEVAS Fermin
DEMATTEIS Erika Michela

Local Contact: LAVERSENNE Laetitia

Samples: $TiFe_{0.85}Mn_{0.05}D_2$

Instrument	Req. Days	All. Days	From	To
D1B	1	1	26/08/2020	26/08/2020

Abstract:

TiFe(Mn) is a promising system for H2 storage with a di-hydride having a gravimetric capacity of 1.86 wt.% H2. Upon hydrogen absorption, consecutive formation of monohydride beta-TiFe(Mn)H and dihydride gamma-TiFe(Mn)H2 occurs. The phase transformations have been successfully characterized by in-situ neutron diffraction analysis on D1B during deuteration of the TiFe0.85Mn0,05 while recording the Pressure-Composition Isotherms (PCI) at RT between 0.1 < PD2 < 100 bar (proposal CRG 5-22-201). However, the two hydrides crystallize in orthorhombic structures with different space groups: P2221 and Cmmm for beta- and gamma-phases respectively. In addition, two different beta-phases have been reported, with composition and occurrence depending on sample history. For all these structures, hydrogen atoms are in octahedral sites. The D1B experiment allowed to characterize the phase transitions but not to fully solved the structure of the gamma-dihydride due to low resolution of D1B at high angles. Therefore, acquisition of high-resolution data for the dihydride have been done to fully solve the structure and to completely analyse the in-situ neutron diffraction data collected on D1B.

Introduction

TiFe crystallizes in a CsCl-type cubic structure (S.G. *Pm-3m*).[1] Its lattice parameter can vary because of composition fluctuations within the homogeneity domain of the TiFe phase.[2] Upon hydrogenation, TiFe forms two hydrides adopting orthorhombic structures: the monohydride TiFeH (β phase), and the dihydride $TiFeH_2$ (γ phase). The PCI curves under deuterium of TiFe present two distinguished plateau pressures that correspond to the formation of β- (1st plateau) and γ-phase (2nd plateau).[3] Usually the two plateaus are better defined upon desorption.[4] For absorption, the formation of a solid solution of H(D) in TiFe is firstly observed (α phase).[5] The solid solution α has a maximum H(D) solubility at $H/M = 0.04$ (corresponding to $TiFeH_{0.08}$). Then, through the first plateau, the β phase forms (S.G. $P222_1$),[6] even if discrepancies concerning the TiFe hydride crystal structures is still present in the literature. In fact, controversial results report other orthorhombic structures (S.G. *C222*) for this phase.[7] and an orthorhombic structure for the dihydride (γ phase; S.G. *Cmmm*).[8]

The hydride $TiFe_{0.85}Mn_{0.05}D_{1.7}$ has been studied at ILL by *high resolution* Neutron Diffraction (ND) on D2B to determine its crystal structure at room temperature (RT). The sample was previously loaded in a stainless-steel container then submitted to deuterium pressure with a manual Sievert's type volumetric rig provided by ICMPE/CNRS. ND-pattern of the sample was recorded after deuterium pressure was applied (ca. 9 MPa; 1.7 D/f.u.) to complete deuteration to the γ phase.

As it can be observed **Fig.1**, the γ phase has been obtained and the phase structure can be well described in the orthorhombic *Cmmm* space group. Results of the refinement are given in **Table 1**.

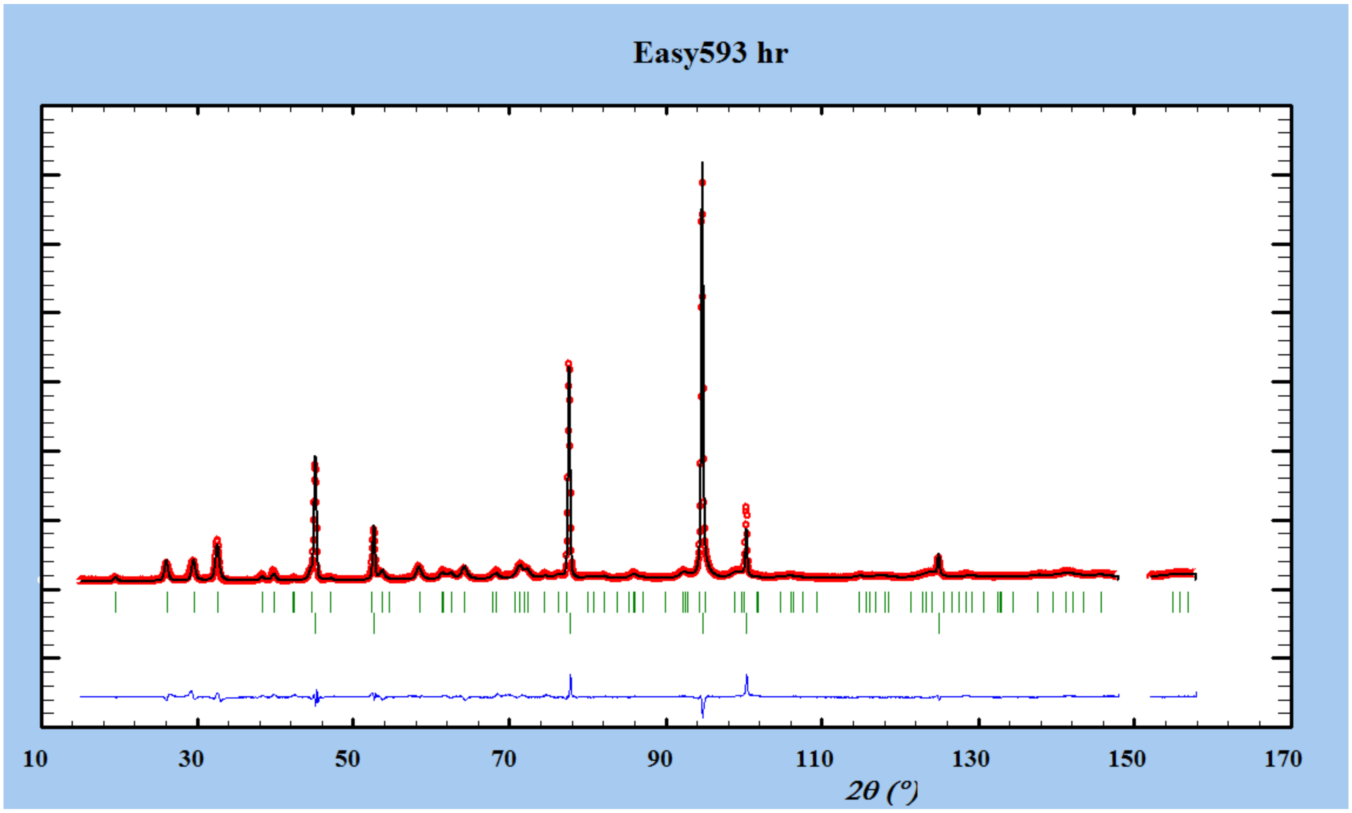

Figure 1 *– ND diffraction pattern of the deuteride* $TiFe_{0.85}Mn_{0.05}D_2$ *collected in HR mode on D2B. Observed, calculated and difference curves are shown. The first set of lines correspond to the deuteride whereas the second set is attributed to the stainless-steel container.*

Table 1 *– Results from Rietveld refinement of the deuteride* $TiFe_{0.85}Mn_{0.05}D_2$.

Name	*Wyckoff pos.*	*x*	*y*	*z*	*B*	*Occ.*	*Mult.*
Ti	4*j*	0	0.219 (1)	½	0.3	1	4
D3	4*e*	¼	¼	0	0.08(8)	0.901(11)	4
D2	2*c*	½	0	½		0.356(7)	2
D1	2*a*	0	0	0		0.375(6)	2
Fe	4*g*	0.2857(6)	0	0	0.3	0.895	4
Mn						0.053	
Ti						0.053	

Cmmm space group; cell parameters: a= 6.2469(4); b= 7.0633(4); c=2.8399(1) Å

R_p=4.43%; R_{wp}=6.41%; R_{exp}=1.26%; R_{Bragg}= 7.99%

Conclusion

Neutron diffraction analysis of the deuteride $TiFe_{0.85}Mn_{0.05}D_{1.7}$ using HR D2B diffractometer demonstrates that this γ phase crystallizes in an orthorhombic structure with space group *Cmmm*. The crystal structure of the deuterated phase is correctly described by a partial substitution of Fe by Ti and Mn on the Wyckoff position 4*g* and by partial interstitial filling of the sites 2*a*, 2*c* and 4*d* with deuterium. The composition obtained by refinement (1.63(2) D/f.u.) is in fair agreement with the one measured by the volumetric uptake. These data will be further used to complete the analysis of the in-situ experiment performed on D1B (proposal **5-22-771).**

References

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