

# Influence of hydrogen insertion on the magnetic properties of the $RFe_{11}Ti$ phases

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## Abstract

Insertion of hydrogen atoms within the crystal structure induces a significant modification of the physical properties. A moderate unit cell increase and a large increase of the Curie temperature is found. Other properties such as the magnetocrystalline anisotropy are also affected by H insertion within the lattice. Combining magnetisation measurements, a.c. susceptibility and thermomagnetic analysis, the magnetic phase diagrams of the  $RFe_{11}TiH$  compounds are established. The competition between the magnetocrystalline anisotropy terms leads to spin reorientation phenomena in  $RFe_{11}TiH$  with  $R=Er$  or  $Ho$ . For  $R=Tb$  and  $Dy$  the spin reorientation transitions observed in the  $RFe_{11}Ti$  compounds have disappeared.

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## 1. Introduction

There exist quite an extensive class of materials of the type  $RFe_{12-x}M_x$  where  $M=Ti, Cr, V,$  or  $Mo$  retaining the  $ThMn_{12}$  structure [1]. These series of intermetallics offer two main advantages as hard magnetic material: (i) a high Fe content that favours a high magnetisation; and (ii) a relatively high Curie temperature, in particular for the Ti containing compounds. The insertion of hydrogen in intermetallic phases exhibiting hard magnetic properties such as the  $R_2Fe_{14}B$ , the  $R_2Fe_{17}$  phases has attracted much interest in the last two decades [2,3]. In particular, the magnetic properties of the  $R_2Fe_{17}$  compounds have been found to be very sensitive to the presence of interstitial atoms [2]. Here, the analysis will focus on the influence of H insertion on the structural and magnetic properties of the  $RFe_{11}Ti$  compounds.

## 2. Experimental

The alloys have been obtained by melting the high

purity starting elements (better than 99.95%) in a high frequency induction furnace equipped with a water cooled copper crucible. The homogeneity of the ingot was subsequently achieved by annealing at 950 °C for 10 days. The hydrogen insertion has been carried out under 20 bars of  $H_2$  gas and short thermal activation was needed to initiate the reaction. The hydrogen content has been determined by a gravimetric method. The lattice parameters were derived from X-ray diffractometry. Thermomagnetic analysis of the sample being sealed in a silica tube to avoid oxidation or hydrogen release, was performed using a Faraday type balance.

The low temperature a.c. magnetic susceptibilities have been obtained on a computer controlled mutual inductance susceptometer in an exciting field of 1 Oe and a frequency of 120 Hz. A lock-in amplifier was used to measure the complex susceptibility,  $\chi_{ac}=\chi'-j\chi''$ , where  $\chi'$  is the initial susceptibility, a quantity which is related to the variation in the sample magnetisation, and  $\chi''$  is non zero if magnetic energy is absorbed by the sample. The temperature dependence of the real component ( $\chi'$ ) and the imaginary component ( $\chi''$ ) of the a.c. susceptibility were measured in order to determine the onset temperatures of the magnetic phase transitions. The measurements of the real part of the a.c. susceptibility are very sensitive to the

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onset of the magnetic phase transition caused by the change of the anisotropy energy.

### 3. Results and discussion

The synthesis has led to the formation of stable hydrides. These compounds crystallise in a tetragonal structure of space group  $I4/mmm$ . The hydrogen content determined by gravimetric method is about one H atom per  $RFe_{11}Ti$  formula unit. This value is in excellent agreement with earlier neutron diffraction investigations [4,5] which have shown that hydrogen atoms enter the  $2b$  interstitial site. A full occupancy of this  $2b$  site leads to a maximum H content of one atom per formula unit. The hydrogen insertion within the crystal structure induces a significant increase of the unit cell. The lattice parameters deduced from X-ray diffraction are summarised in Table 1. The volume increase upon hydrogen insertion does not exceed  $2 \text{ \AA}^3$  on average per inserted hydrogen atom. The largest cell increase:  $1.95 \text{ \AA}^3$  is observed for the  $CeFe_{11}Ti$  compound, a result which can probably be explained by the progressive Ce valence change that occurs upon hydrogen insertion within the lattice. Indeed, it has been shown by X-ray absorption spectroscopy that the Ce valence state changes upon H insertion in  $CeFe_{11}Ti$  [6]. Hydrogen insertion in the  $RFe_{11}Ti$  compounds induces a unit cell volume increase of 1%. This value is much smaller than the up to 4% reported for  $R_2Fe_{17}H_x$  and  $R_2Fe_{14}BH_x$  compounds [2,3]. This rather moderate cell expansion has two origins:

- first, the hydrogen content is low. Indeed, only one H atom per R atom in the  $RFe_{11}Ti$  compounds against more than two H atoms per rare-earth in both the  $R_2Fe_{17}H_x$  and  $R_2Fe_{14}BH_x$  compounds.
- second, as discussed above the mean unit cell expansion

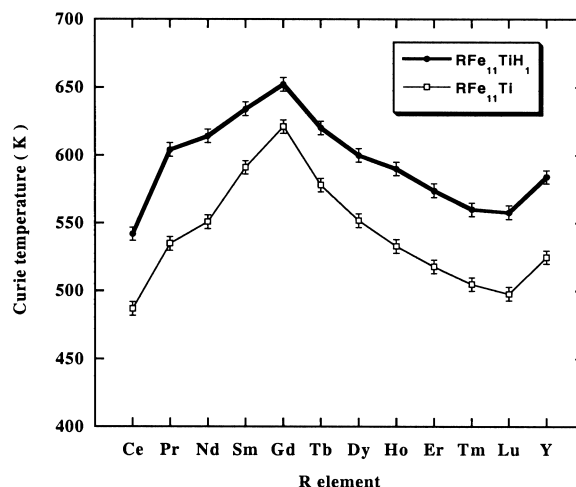


Fig. 1. Curie temperatures of the  $RFe_{11}Ti$  and  $RFe_{11}TiH$  compounds.

upon hydrogen insertion is only about  $1.7 \text{ \AA}^3$  in the  $RFe_{11}Ti$  phases against an increase of about  $2.3 \text{ \AA}^3$  in other iron rich intermetallics such as  $R_2Fe_{17}H_x$  and  $R_2Fe_{14}BH_x$  compounds.

This rather moderate unit cell expansion in comparison with the related  $R_2Fe_{17}H_x$  phases originates from the more compact structure of the  $RFe_{11}Ti$  compounds. Indeed, in the  $R_2Fe_{17}H_x$  phases only one rare-earth of every three have been replaced by two iron atoms forming a dumbbell pair whereas in the  $RFe_{11}Ti$  structure one half of the rare-earths of the original  $CaCu_5$  structure type have been replaced by a pair of transition metal elements.

As can be seen from Fig. 1, the Curie temperature ( $T_C$ ) of the  $RFe_{11}Ti$  phases is increased upon hydrogen insertion. This increase is larger for the non magnetic rare-earth elements such as Y, Lu or Ce and is much smaller for the Gd $Fe_{11}Ti$  phase. It is to be mentioned that the Curie temperatures reported in Fig. 1 have to be regarded as underestimation of the  $RFe_{11}TiH$  Curie temperatures since hydrogen starts to leave the crystal structure below the

Table 1

Lattice parameters of the  $RFe_{11}Ti$  and  $RFe_{11}TiH$  compounds as deduced from X-ray diffraction

R element	$RFe_{11}Ti$			$RFe_{11}TiH_{1-\delta}$		
	$a$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )	$a$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )
Ce	8.540 (1)	4.780 (1)	348.5	8.566 (1)	4.802 (1)	352.4
Pr	8.609 (2)	4.798 (1)	355.6	8.610 (2)	4.817 (1)	357.1
Nd	8.574 (2)	4.794 (1)	352.4	8.583 (2)	4.815 (1)	354.7
Sm	8.558 (1)	4.789 (1)	350.8	8.573 (1)	4.808 (1)	353.4
Gd	8.530 (1)	4.788 (1)	348.5	8.554 (1)	4.804 (1)	351.5
Tb	8.515 (1)	4.790 (1)	347.3	8.548 (1)	4.803 (1)	351.0
Dy	8.505 (1)	4.789 (1)	346.4	8.537 (1)	4.798 (1)	349.8
Ho	8.491 (1)	4.784 (1)	345.0	8.525 (1)	4.794 (1)	348.4
Er	8.481 (1)	4.783 (1)	344.1	8.519 (1)	4.791 (1)	347.6
Tm	8.476 (1)	4.786 (1)	343.8	8.510 (1)	4.787 (1)	346.7
Lu	8.462 (1)	4.779 (1)	342.2	8.501 (1)	4.783 (1)	345.7
Y	8.509 (1)	4.790 (1)	346.8	8.535 (1)	4.797 (1)	349.4

Curie temperature. The increase of the Curie temperature reflects the increase of the Fe–Fe exchange interactions induced by the unit cell expansion that occurs upon hydrogenation [4]. According to Arnold and co-workers [7], the Curie temperature of the  $\text{NdFe}_{11}\text{Ti}$  phase is very sensitive to an applied pressure,  $\Delta T_c/\Delta P = -2.7$  K/kbar. Hydrogen insertion induces a  $T_c$  increase of 63 K. We can thus derive the interstitial insertion-induced ‘negative’ pressure on the host compound as ca.  $-23$  kbar per inserted H atom. It is worth to note that in spite of the close relationship between the two  $\text{R}_2\text{Fe}_{17}$  and  $\text{RFe}_{11}\text{Ti}$  structures the pressure effect of hydrogen insertion is twice larger in the  $\text{RFe}_{11}\text{Ti}$  structure. Similar analyses of the influence of the C or N insertion on the Curie temperature also evidence a larger sensitivity of the  $\text{RFe}_{11}\text{Ti}$  compounds than of the  $\text{R}_2\text{Fe}_{17}$  compounds [8]. This large sensitivity of the  $\text{RFe}_{11}\text{Ti}$  Curie temperature to the presence of interstitial element probably results from the character of the  $\text{RFe}_{11}\text{Ti}$  crystal structure.

The overall magnetisation of the  $\text{RFe}_{11}\text{Ti}$  compounds is only slightly increased upon hydrogen insertion. Because of the significant increase of the Curie temperature the increase is larger at room temperature than at 4 K where the magnetisation of the  $\text{RFe}_{11}\text{Ti}$  phases and of the hydrides are very close. The average iron magnetic moment in the  $\text{RFe}_{11}\text{Ti}$  phases is about  $1.7$  to  $1.8\mu_B$  per iron atom. After hydrogenation, the iron magnetic moments remains of the same magnitude  $1.8$ – $1.9\mu_B$  (for more details see Refs. [4,9]). Unlike the large magnetisation increase occurring in the  $\text{R}_2\text{Fe}_{17}$  or the  $\text{R}_2\text{Fe}_{14}\text{B}$  compounds, the magnetisation change upon hydrogen insertion in the  $\text{RFe}_{11}\text{Ti}$  phase is remarkably small.

All the  $\text{RFe}_{11}\text{Ti}$  compounds with  $\text{R}=\text{Y}, \text{Lu}, \text{Tm}, \text{Gd}, \text{Sm},$  or  $\text{Ce}$  exhibit an axial ( $c$ -axis) easy magnetisation direction (EMD), whatever the temperature. As can be seen from Fig. 2, this axial preference is kept after hydrogen insertion. This proves that the iron sublattice anisotropy remains axial after H insertion. The H induced evolution of the Fe sublattice anisotropy field has been reported elsewhere [4,9]. In the case of the Sm containing compound, the large magnetocrystalline anisotropy has been found to be improved upon H insertion [10,11]. Thermomagnetic behaviour of the  $\text{TbFe}_{11}\text{Ti}$  and  $\text{TbFe}_{11}\text{TiH}$  are compared in Fig. 3. An anomalous behaviour is observed below  $100^\circ\text{C}$  in  $\text{TbFe}_{11}\text{Ti}$ , an anomaly which is associated to the spin reorientation behaviour. A spin reorientation temperature (SRT) manifests itself by a rotation of the EMD. In  $\text{TbFe}_{11}\text{Ti}$ , the magnetic moments are aligned along the  $c$ -axis of the tetragonal structure above this SRT whereas below this temperature the magnetic moments are aligned in the  $(a,b)$  basal plane. This reorientation of the magnetic moment is no longer observed after hydrogen insertion in  $\text{TbFe}_{11}\text{Ti}$ . Only a progressive increase of the magnetisation up to the Curie point is observed in the thermomagnetic curve of  $\text{TbFe}_{11}\text{TiH}$ . This increase results from the decrease of the

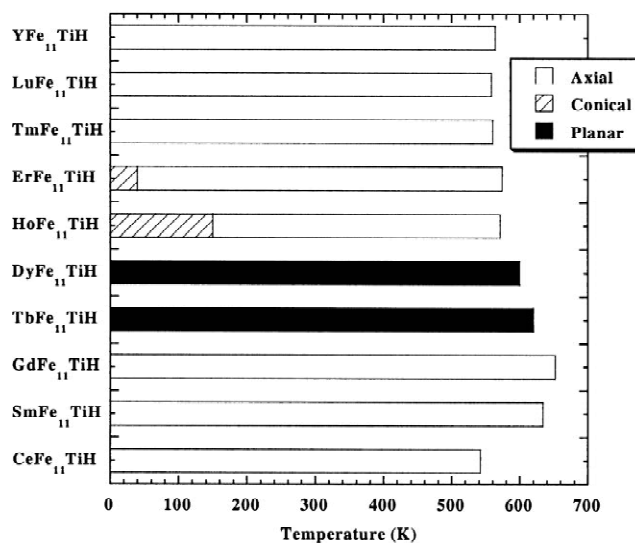


Fig. 2. Observed temperature variation of the magnetic structures of the  $\text{RFe}_{11}\text{TiH}$  series as deduced from a.c. susceptibility and thermomagnetic investigations.

Tb sublattice magnetisation, a magnetisation coupled anti-ferromagnetically with the dominant Fe one. a.c. susceptibility measurements on  $\text{ErFe}_{11}\text{TiH}$  exhibit a SRT below 50 K. This behaviour is very close to that observed for the uncharged  $\text{ErFe}_{11}\text{Ti}$  compounds. The a.c. susceptibility measurements performed on  $\text{HoFe}_{11}\text{TiH}$  exhibit a maximum at about 150 K, Fig. 4. Such phenomenon has not been reported for the corresponding  $\text{HoFe}_{11}\text{Ti}$  compound whose magnetic moments remains aligned along the  $c$ -axis of the crystal structure up to the ordering temperature. The origin of the anomalous behaviour of the  $\text{HoFe}_{11}\text{TiH}$  susceptibility has been extensively studied by neutron diffraction investigation [5,12,13]. We have shown that in  $\text{HoFe}_{11}\text{TiH}_x$  compounds the magnetic moments are tilted away from the  $c$ -axis with a tilt angle which increases

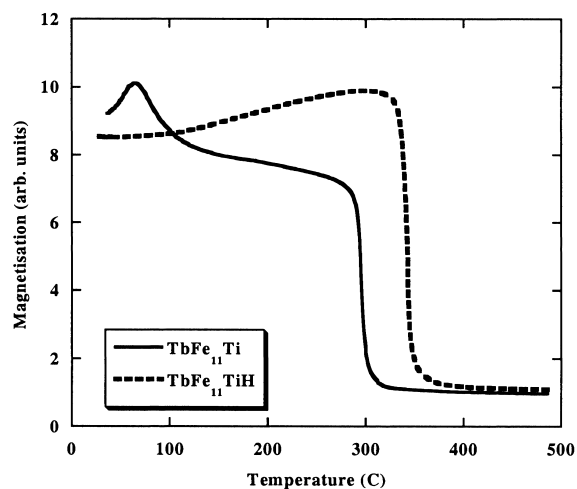


Fig. 3. Thermal variations of the d.c. magnetic susceptibilities recorded for  $\text{TbFe}_{11}\text{Ti}$  and  $\text{TbFe}_{11}\text{TiH}$  compounds.

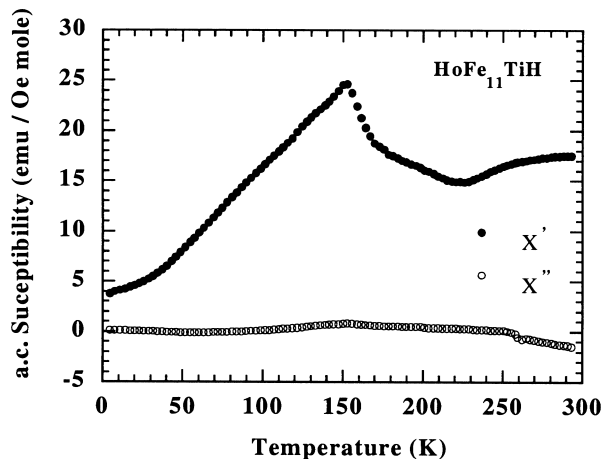


Fig. 4. Temperature dependence of the real,  $\chi'$  and imaginary,  $\chi''$ , portions of the a.c. magnetic susceptibility of  $\text{HoFe}_{11}\text{TiH}$ .

dramatically at the SRT (about 150 K). This hydrogen induced SRT in  $\text{HoFe}_{11}\text{Ti}$  evidences that below 150 K the magnetocrystalline anisotropy of the Ho sublattice dominates over the Fe one. Indeed, as discussed above the preference of the Fe sublattice for the  $c$ -axis is kept after hydrogen insertion. The relative increase of the Ho sublattice anisotropy originates from the increase of the crystal electric field parameter experienced at the rare-earth nuclei. Indeed, the absolute value of the second order crystal electric field parameter also called  $A_2^0$  has been found to increase significantly upon hydrogen insertion within the lattice [14,15].

The magnetic structure of  $\text{DyFe}_{11}\text{Ti}$  has been widely investigated [16,17]. Particular attention has been paid to the investigation of the spin reorientation phenomena occurring below 300 K. The gradual character of the first-order SRT in  $\text{DyFe}_{11}\text{Ti}$  has been a matter of discussion [18]. According to more recent investigations [17,18], two successive transitions are observed in  $\text{DyFe}_{11}\text{Ti}$ , a second-order transition at 191 K and a first-order transition at about 52 K. The magnetic structure of the corresponding hydride has been less studied. A first investigation was reported [19] for  $\text{DyFe}_{11}\text{TiH}_{1.4}$  followed by a more detailed investigation of the  $\text{DyFe}_{11}\text{TiH}_x$  phases [20] and a magnetic phase diagram reported by Nikitin et al. [21]. In their study Zhang et al. [19] have reported two spin reorientation temperatures. By a systematic investigation of the  $\text{DyFe}_{11}\text{TiH}_x$  phases it has been shown [20] that the two SRT occurring for low hydrogen concentration disappear for hydrogen concentrations higher than 0.8 [20]. As a consequence, the magnetic moments were supposed to lie in the (001) plane whatever the temperature. In the present study, no peculiar behaviour has been observed for  $\text{DyFe}_{11}\text{TiH}$  neither in the a.c. susceptibility measured between 4 and 300 K nor in the thermomagnetic investigation carried out above room temperature. It is thus

believed that the magnetic moments do not undergo a spin transition in  $\text{DyFe}_{11}\text{TiH}$ . We have already discussed that in the  $\text{RFe}_{11}\text{TiH}$  phases the rare-earth contribution to the anisotropy is enhanced upon hydrogen insertion. Consequently, the incorporation of hydrogen in  $\text{DyFe}_{11}\text{Ti}$  may increase the temperature range in which the magnetocrystalline anisotropy of the rare-earth sub-lattice dominates over that of the iron sub-lattice and the magnetic moment should lie in the (001) plane in the whole temperature range. In order to verify this hypothesis, a complete analysis of the thermal evolution of the  $\text{DyFe}_{11}\text{TiH}$  magnetic structure will be carried out using neutron diffraction [22].

To conclude, the magnetic phase diagram of the  $\text{RFe}_{11}\text{Ti}$  compounds are modified upon H insertion. The Curie temperature increase is large, a SRT is induced for  $\text{R}=\text{Ho}$  but it disappears for  $\text{Tb}$ . For permanent magnet applications,  $\text{SmFe}_{11}\text{TiH}$  is the more promising material because of its large Sm sublattice anisotropy. The H induced modifications of the magnetic phase diagrams reflect the modifications of the R atomic environment which induces a change of the second order crystal electric field experienced by the rare-earth nuclei.

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