

Influence of hydrogenation on structure and magnetic properties of $\text{HoFe}_{11-x}\text{Co}_x\text{Ti}$

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Abstract

Magnetic properties and crystal structure of the hydrides of ferromagnetic compounds $\text{HoFe}_{11-x}\text{Co}_x\text{Ti}$ ($x=1, 2, 4, 6, 7, 11$) are investigated. The crystal structure was determined by X-ray diffraction (XRD) analysis and the magnetization was measured in applied magnetic fields up to 10 T and at temperatures ranging from 5 K to room temperature. Results show that the crystal structure of the hydrides is the same as for parent compounds but with a moderate unit cell increase. Other properties such as saturation magnetization are affected by H insertion within the lattice. The effect of hydrogenation on magnetic anisotropy energy leads to disappearance of the FOMPs observed in the parent compounds.

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1. Introduction

The intermetallic compounds with formula $\text{RFe}_{11-x}\text{M}_x$ in which $\text{M}=\text{Ti}, \text{Cr}, \text{V},$ or Mo crystallize in a tetragonal structure with space group $I4/mmm$ (ThMn_{12} type structure) with two formula units per unit cell. Two main interests of these series of 1:12 type compounds as potential hard magnets are the high Fe content thus favoring a high magnetization level and a relatively high Curie temperature, in particular for the Ti containing compounds.

Insertion of light elements such as H, C, and N in the $\text{RFe}_{11-x}\text{M}_x$ compounds was found to induce marked changes on the magnetic properties. During the past 10 years, large efforts were devoted to the 1:12 type hydrides, more particularly on the characterization of $\text{RFe}_{11}\text{TiH}$ systems [1–5]. Parallel, the

effect of Co substitution for Fe on the magnetic properties of $\text{RFe}_{11-x}\text{M}_x$ series were studied as well [6–12]. In particular the influence of Co substitution for Fe was investigated in the here-concerned $\text{HoFe}_{11-x}\text{Co}_x\text{Ti}$ compounds [13]. Co substitution for Fe in these compounds leads to decrease the lattice parameters and has a beneficial effect in increasing the Curie temperature. The aim of this paper is to study the influence of hydrogenation on the crystal structure and the magnetic properties of $\text{HoFe}_{11-x}\text{Co}_x\text{Ti}$.

2. Experimental

The parent compounds were prepared by arc melting good purity elements ($\geq 3\text{N}$) Ho, Fe, Co, Ti under high purity (4N5) Ar atmosphere. To achieve homogeneity of the ingots, the samples were annealed at 1050 °C for 12 days in evacuated silica ampoules.

The hydrides were prepared by inserting ground powder samples in stainless steel autoclaves filled with pure hydrogen gas (5N5) at 20 bar pressure thus maintained at 200 °C for 20 h. The hydrogen content was determined by gravimetric method and the lattice parameters were derived from X-ray diffraction patterns on powdered samples, recorded at room temperature with $\text{Cu}(K\alpha)$ radiation graphite monochromatised in backscattering Bragg–Brentano geometry, the record step being of 0.05°. The lattice parameter refinements were carried out by using a profile refinement analysis.

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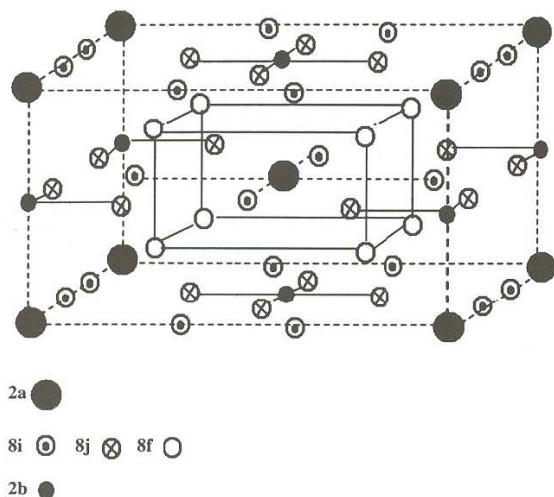


Fig. 1. Schematic representation of the $RTM_{12}X$ unit cell (R refers to rare-earth, TM to transition metal and X to interstitial atoms). R atoms occupy 2a, TM atoms occupy 8i, 8j and 8f and X atoms occupy 2b sites.

Magnetization measurements performed between 5 and 300 K and up to 10 T fields were undertaken using an extraction type magnetometer. The saturation magnetizations were deduced plotting M versus $1/H^2$ [14].

3. Results and discussion

3.1. Cell parameter analysis

It is well known that in $ThMn_{12}$ type of structure the Ho atoms occupy the origin and the center of the tetragonal cell (2a). The Fe atoms totally or partly occupy one or more of the positions 8i ($x, 0, 0$), 8j ($x, 0, 1/2$) and 8f ($1/4, 1/4, 1/4$) as shown in Fig. 1. Because of a most favorable heat of formation of Fe–Ti than Ho–Ti binaries, the Ti atoms occupy preferentially the 8i sites [3]. Moreover since the atomic site of 8f has the smallest volume reference to those of 8i and 8j sites, the Co atoms for increasing Co content occupy 8f sites, however then they occupy 8j and 8i sites, respectively to form energetically favorable Co–Ho bonds

Table 1
Crystal lattice parameters a and c , unit cell volume V , and saturation magnetization for the $HoFe_{11-x}Co_xTi$ ($x = 1, 2, 4, 6, 7, 11$) compounds and their hydrides at room temperature

Compounds	a (Å)	c (Å)	V (Å ³)	$\Delta V/V$ (%)	M_s ($\mu_B/f \times u$)
$HoFe_{10}CoTi$	8.499	4.777	345.057	–	14.88
$HoFe_{10}CoTiH$	8.524	4.783	347.526	0.716	15.71
$HoFe_9Co_2Ti$	8.495	4.773	344.445	–	15.61
$HoFe_9Co_2TiH$	8.511	4.780	346.249	0.524	15.77
$HoFe_7Co_4Ti$	8.468	4.757	341.110	–	15.99
$HoFe_7Co_4TiH$	8.478	4.763	342.348	0.363	15.97
$HoFe_5Co_6Ti$	8.435	4.743	337.461	–	16.07
$HoFe_5Co_6TiH$	8.462	4.748	339.983	0.747	15.38
$HoFe_4Co_7Ti$	8.422	4.736	335.925	–	14.39
$HoFe_4Co_7TiH$	8.440	4.742	337.789	0.555	13.87
$HoCo_{11}Ti$	8.382	4.709	330.845	–	11.62
$HoCo_{11}TiH$	8.395	4.714	332.224	0.412	11.31

[15]. Tomey et al. reported that hydrogen atoms occupy the octahedral 2b site in $Er(Fe, M)_{12}D_x$ [16]. But later reported results indicate that small amounts of hydrogen atoms could occupy either the 16l or the 32o sites [17].

Analysis of X-ray diffraction patterns show that all samples crystallize in the characteristic tetragonal $ThMn_{12}$ structure with space group $I4/mmm$. Results of the structural data are presented in Table 1 and displayed in Fig. 2(a–c). As can be seen, hydrogen insertion experimentally corresponding to $\sim 1H/at$ per formula unit, leads to increase both the cell parameters, a being

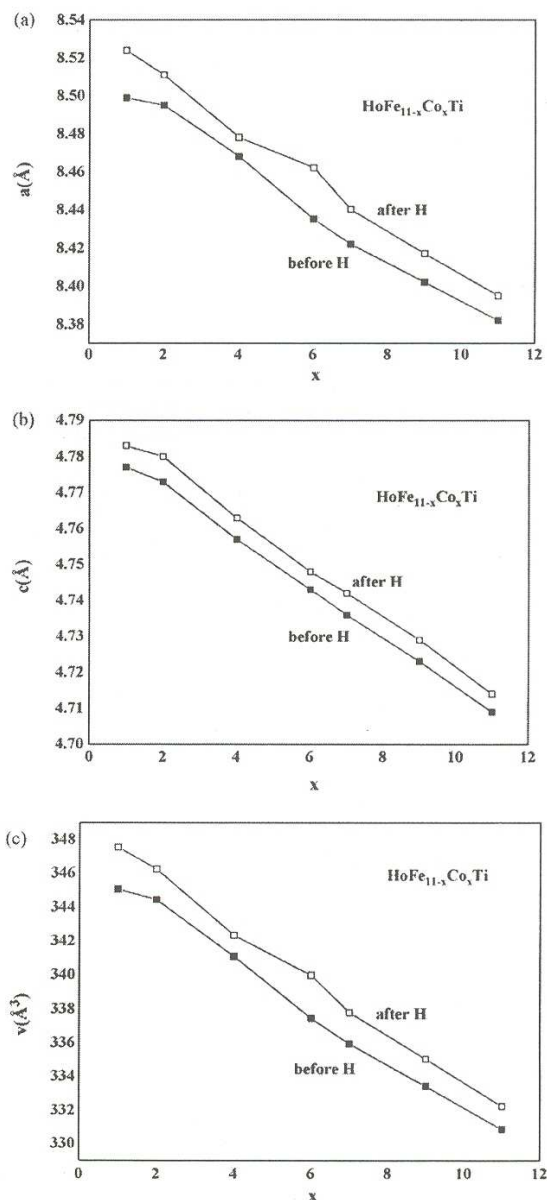


Fig. 2. (a–c) Lattice parameters (a and c) and unit-cell volume (V) for the parent and the hydride compounds vs. x .

slightly more affected than c. Consequently the unit cell volume increases, but the maximum expansion remains limited, of $\Delta V/V=0.75\%$ for $x=6$. If H atoms only occupy the 2b interstitial site, then a full occupancy of these sites leads to a maximum H content of one atom per formula unit whereas there can be up to 2.5 and 2.75 H atoms per rare-earth in the $R_2Fe_{17}H_x$ and $R_2Fe_{14}BH_x$ compounds, respectively. This

is why the volume expansion in 1:12 type remains relatively moderate.

3.2. Magnetization analysis

Field dependence of magnetization of the $HoFe_{11-x}Co_xTi$ ($x=1, 2, 4, 6, 7, 11$) compounds and their hydrides are compared

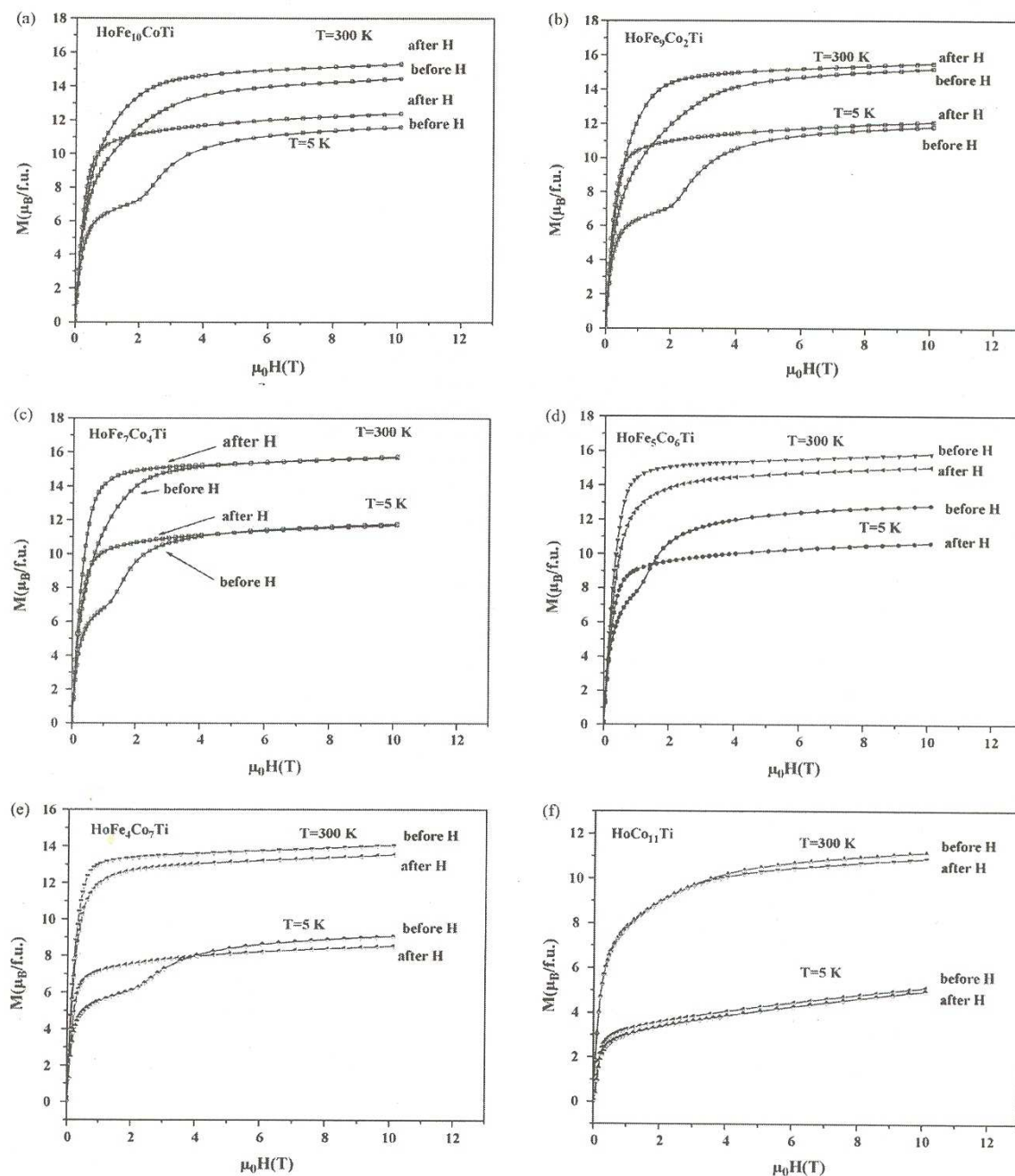


Fig. 3. (a–f) Magnetization versus magnetic field at 5 and 300 K for the hydride and the parent compounds.

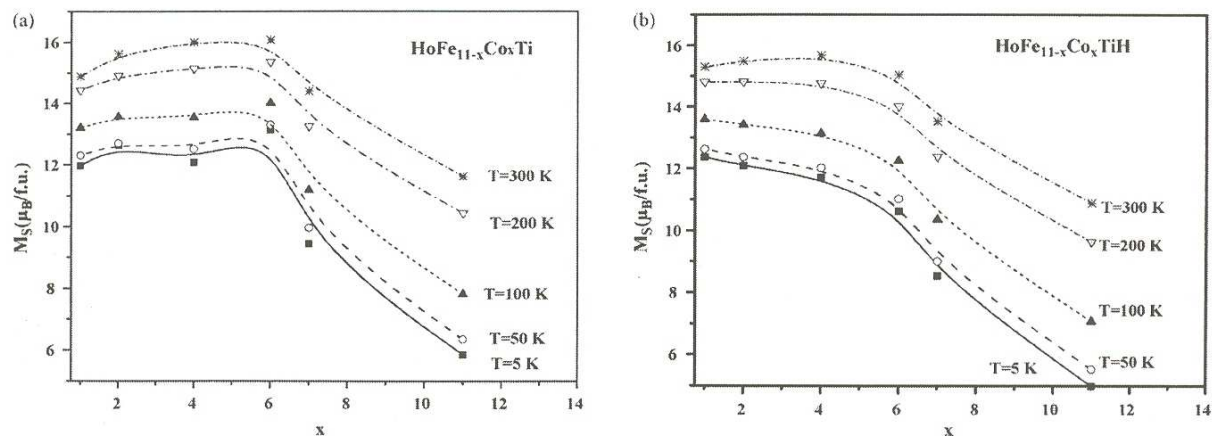


Fig. 4. (a and b) M_s vs. Co content, x , for the parent and the hydride compounds at $T = 5, 50, 100, 200, 300$ K.

in Fig. 3(a)–(f) at temperatures 5 and 300 K all parent samples except $\text{HoCo}_{11}\text{Ti}$ exhibit a first order magnetization process (FOMP) at 5 K but it is fully suppressed in the hydride traces. The origin of the FOMP in the $\text{RFe}_{12-x}\text{M}_x$ compounds is well understood [6,18] in terms of competing anisotropy between the Fe axial contribution and the R contribution which is of planar type provides that the second order Stevens coefficient $\alpha(\text{R})$ is negative as it is for $\text{R} = \text{Ho}$. At low temperature, the $\text{R} = \text{Ho}$ contribution dominates thus leading to stabilize a ferrimagnetic – since Ho belongs to the second series of rare-earth with $J = L + S$, S_{R} and S_{3d} , being opposite – planar or cone-type magnetic structure. Closer to room temperature, the Ho type contribution to magnetocrystalline anisotropy is markedly weakened comparison made to those of Fe, in parallel the strength of the R moment decreased more than those of the Fe ones. Consequently, the ferrimagnetic structure is almost of axial-type, with a reinforced magnetization for similar applied magnetic fields as shown in Fig. 3(a–e). For intermediate temperature, application of larger and larger magnetic fields gives rise to the FOMP. For the corresponding hydrides, the situation is made more simple since insertion of hydrogen in the $\text{RFe}_{12-x}\text{M}_x$ compounds is known to reinforce the axial character of the Fe sublattice contributions to the total magnetocrystalline anisotropy terms (magnetocrystalline constant $K_1 \uparrow$), but to markedly reduce (but increase) the contributions of the R sites if $\alpha(\text{R})$ is negative (but positive) [18]. So for $\text{R} = \text{Ho}$, the corresponding hydrides do not exhibit the FOMP, even to the lowest temperature, the magnetic structure being transformed to axial or conical-type along the c axis.

Here it is worth to note that for the compounds the critical field for the FOMP decreases from $H \sim 2.5$ T to 1 T when x_{Co} (the Co content in $\text{HoFe}_{11-x}\text{Co}_x\text{Ti}$ compounds) varies from 1 to 6. However, the critical field takes again a larger values for $x_{\text{Co}} = 7$ with $H_{\text{FOMP}} \sim 2.5$ T.

Fig. 4 shows the variation at different temperatures of the saturation magnetization M_s versus x_{Co} for both the compounds and their corresponding hydrides. It is clear that for the $\text{HoFe}_{11-x}\text{Co}_x\text{Ti}$ compounds M_s increases whatever is the temperature, from $x_{\text{Co}} = 1$ to 6. For example, at $T = 300$ K, M_s varies from 14.8 to $16.1 \mu_B/f.u.$ It appears that for the ferri-

magnetic type of $M_{\text{R}}-m_{3d}$ couplings the reinforcement of M_s originates from the progressive increase of the mean transition metal moment (m_{3d}) when x_{Co} increases up to 6 as seen in Fig. 5, thus leading to a reduction of H_{FOMP} , as shown in Fig. 3(a)–(d).

The maximum in all M_s versus x_{Co} curves is consistent with the Pauling–Slater curve and can be explained in terms of a rigid band model. In the Fe–Co binary system with increasing substitution of Co for Fe the spin-up d band is filled at first. Hence the difference between the spin-up and spin-down states increases. When the spin-up band is completely filled, there will be installed a strong ferromagnetism state. Then the spin-down band begins to be filled, so the difference between spin-up and spin-down states diminishes, which results a reduction in the saturation magnetization [11,14,18]. As shown in Figs. 4(a) and (b) and 5, for $x_{\text{Co}} \geq 7$, the saturation magnetization markedly drop down upon the conjugate effects of the down states band filling and the opposite moment M_{R} to $\langle m_{3d} \rangle$.

The saturation magnetizations of all compounds before and after hydrogenation are given in Table 1. Moreover in Fig. 5, a comparison of the M_s values is made for the compounds and

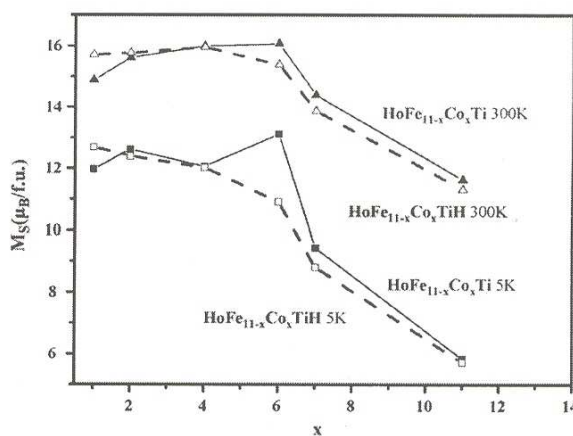


Fig. 5. M_s vs. Co content, x , for the parent and the hydride compounds at $T = 5, 300$ K.

their corresponding hydrides. It was shown that hydrogen insertion causes to increase slightly M_s for $RFe_{12-x}M_x$ [16–19], but increasing the Co content leads M_s to decrease. In ferromagnetic (ferrimagnetic) Co-based intermetallic compounds, hydrogen absorption leads to dramatically lower the local Co moment [20]. The change of the magnetic properties in the Fe compounds occurs in the opposite direction from those in the Co compounds.

Finally, back to the Fig. 3(e and f) it appears that the H_{FOMP} was increased again up to ~ 2.5 T, e.g. $x_{Co} = 7$. This should be due to the fact that in the cobalt containing $R(Fe-Co)_{12-x}M_x$ systems the magnetocrystalline anisotropy constant K_1 is positive for Fe (axial behavior) and negative for Co (basal plane behavior) [7]. This definitively favors a basal plane type structure, reinforced by the Ho own contribution, probably definitively installed for $x_{Co} = 11$ as shown in Fig. 3f for $HoCo_{11}Ti$. Correspondingly, the $HoCo_{11}TiH$ hydride reveals a markedly reinforced anisotropy field up to $H_{AN} \sim 4$ T contrarily to the case of $HoFe_4Co_7TiH$.

4. Summary and conclusions

In this work, the structural and magnetic properties of $HoFe_{11-x}Co_xTiH$ ($x = 1, 2, 4, 6, 7, 11$) have been investigated. It is found that the hydrides retain the $ThMn_{12}$ type structure, but with an increase of unit-cell volume. Magnetic measurements show that insertion of hydrogen enhances the saturation magnetization (M_s) of $HoFe_{11}Ti$ whereas in the other compounds with increasing cobalt contents, M_s decreases. Moreover hydrogen insertion causes to diminish the FOMP in the curve of magnetization versus magnetic field which have been observed in the parent samples at low temperature. The first order transition occurs between two non-equivalent minima of the free energy of the crystals, so hydrogen insertion changes the magnetocrystalline anisotropy energy in such a way that one of the minima disappears [21].

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