

Structural study and magnetic characterization of  $\text{Th}_2\text{Fe}_{17}\text{D}_5$ ,  $\text{Th}_2\text{Fe}_{17}\text{C}_x\text{H}_{5-x}$  and  $\text{Th}_2\text{Fe}_{17}\text{N}_3$

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## Structural study and magnetic characterization of $\text{Th}_2\text{Fe}_{17}\text{D}_5$ , $\text{Th}_2\text{Fe}_{17}\text{C}_x\text{H}_{5-x}$ and $\text{Th}_2\text{Fe}_{17}\text{N}_3$

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**Abstract.** We report on the Rietveld analysis of neutron powder diffraction data recorded on  $\text{Th}_2\text{Fe}_{17}\text{D}_5$ ,  $\text{Th}_2\text{Fe}_{17}\text{C}_{0.6}\text{H}_{4.4}$  and  $\text{Th}_2\text{Fe}_{17}\text{N}_3$ , at 4 K and 300 K. We have determined the crystal structures and magnetic structures of these ternary interstitial compounds. The results are compared to those obtained for  $\text{Th}_2\text{Fe}_{17}$ ,  $\text{Th}_2\text{Fe}_{17}\text{C}_x$  and other related ternary rare-earth compounds. We show that there exist several analogies in the magnetic properties between this series and the  $\text{R}_2\text{Fe}_{14}\text{B}(\text{C})$  series, despite the differences in their respective crystal structures. The size of the iron moments is discussed in terms of interatomic metal-metal distances as well as in terms of the Fe-X (X = N, C or H) bonds.

### 1. Introduction

During the past few years, many investigations have been devoted to rare-earth-transition-metal alloys, mainly the binary intermetallic series such as  $\text{R}_2\text{Fe}_{17}$ ,  $\text{RFe}_7$ ,  $\text{R}_6\text{Fe}_{23}$  or  $\text{RFe}_2$ .

The discovery of the  $\text{R}_2\text{Fe}_{14}\text{B}$  compounds reported by Sagawa *et al* [1] and Croat *et al* [2] in 1984 formed the beginning of a new area for potential permanent magnet materials. A direct development was the investigation of other ternary phases formed as solid solutions of  $\text{R}_x\text{Fe}_y$  alloys and several light elements. Up to now, several families have been studied, mainly derived from the  $\text{R}_2\text{Fe}_{17}$  and the  $\text{RM}_{12}$  alloys by combining them with hydrogen [3, 4], nitrogen [5, 6] or carbon [7-9] leading to formulae  $\text{R}_2\text{Fe}_{17}\text{X}_x$  and  $\text{RM}_{12}\text{X}_x$  (X = H, C, N). All the light elements were found to dramatically increase the Curie temperature and the magnetization. For the carbides and nitrides, a strong enhancement of the rare-earth anisotropy terms was also observed.

Neutron diffraction investigations have played a major role in the study of the  $\text{R}_2\text{Fe}_{14}\text{B}$  and  $\text{R}_2\text{Fe}_{14}\text{C}$  compounds and nowadays they are very helpful for studying the off-stoichiometric  $\text{R}_2\text{Fe}_{17}\text{X}_x$  and  $\text{RFe}_{12}\text{X}_x$  solid solutions. Compared with x-ray diffraction, this technique offers two main advantages:

- (i) it permits us to determine accurately the location of the light elements in the lattice,
- (ii) it enables us to determine accurately the local magnetic moments.

In this paper, we focus attention on the effects of X (N, C and H) on the crystal and magnetic structures of  $\text{Th}_2\text{Fe}_{17}\text{X}_x$  compounds. We describe the synthesis of these ternaries, and use neutron diffraction data to determine at what positions the light elements are located and how their presence affects the size of the magnetic moments determined. The experimental data obtained for  $\text{Th}_2\text{Fe}_{17}\text{X}_x$  will be compared to those of  $\text{R}_2\text{Fe}_{17}\text{X}_x$ ,  $\text{R}_2\text{Fe}_{14}\text{B}$  and  $\text{R}_2\text{Fe}_{14}\text{C}$  compounds and general features of all these iron-rich rare-earth ternaries containing a p element such as C, N or B will be discussed.

## 2. Experimental details

### 2.1. Synthesis

**2.1.1. Alloys and carbides.** The starting alloy  $\text{Th}_{12}\text{Fe}_{17}$  and the parent carbide  $\text{Th}_2\text{Fe}_{17}\text{C}_{0.6}$  were synthesized by using the arc-melting technique. The samples were annealed at  $1100^\circ\text{C}$  for about two weeks and then water quenched. All the samples were checked by x-ray diffractometry using  $\text{Cu K}\alpha$  radiation and a backscattering graphite monochromator set-up. The compounds were found to be single phase having the rhombohedral  $\text{Th}_2\text{Zn}_{17}$  structure type.

**2.1.2. Nitrides.** Prior to nitrogenation, the starting  $\text{Th}_2\text{Fe}_{17}$  alloys were crushed and sieved down to a typical particle size of  $20\ \mu\text{m}$ . A new 'high'-pressure nitrogenation process was used, the details of which have been described elsewhere [10]. The solid-gas reaction was performed under 15 MPa in a stainless-steel autoclave. The purity of the nitrogen gas used was 5N5. Activation of the reaction was completed by heating the powder for several hours at temperature ranging from  $250^\circ\text{C}$  to  $350^\circ\text{C}$ . A first estimation of the N content, obtained by a gravimetric method, leads to  $3.0 \pm 0.1$  N atoms per formula unit. This is a higher N concentration than reached in previous investigations [6, 7].

**2.1.3. Hydrides.** Hydrogenation of the  $\text{Th}_2\text{Fe}_{17}$  and the  $\text{Th}_2\text{Fe}_{17}\text{C}_{0.6}$  ingots was performed in a stainless-steel autoclave under a hydrogen (or deuterium) gas pressure of about 5 MPa leading to stable hydrides or carbohydrides respectively. For  $\text{Th}_2\text{Fe}_{17}\text{X}_5$ ,  $\text{D}_2$  was used preferentially instead of  $\text{H}_2$  due to its lower neutron incoherent cross section. However, as D and C have similar neutron scattering lengths ( $0.667$  and  $0.6648 \times 10^{-15}$  m respectively), we have used H for  $\text{Th}_2\text{Fe}_{17}\text{C}_{0.6}\text{H}_{4.4}$  in order to improve the contrast between the two light elements ( $0.374 \times 10^{-15}$  m for H). The D and H uptakes were determined by volumetric and gravimetric methods.

### 2.2. Neutron diffraction experiments

Neutron diffraction experiments were carried out at the Siloé reactor of the Centre d'Etudes Nucléaires de Grenoble (CENG). DN5, the instrument used, is equipped with a large one-dimensional curved detector (800 cells), allowing us to record a pattern over a range of  $2\theta = 80^\circ$ , and operating either at  $2.49\ \text{Å}$  or  $1.34\ \text{Å}$ . The diffraction data were analysed using the Rietveld technique implemented in the program FULLPROF developed at the Institut Laue-Langevin. Figures 1 and 2 represent the diffraction patterns of  $\text{Th}_2\text{Fe}_{17}\text{N}_3$  and  $\text{Th}_2\text{Fe}_{17}\text{C}_{0.6}\text{H}_{4.4}$ , recorded at 300 K and 4.2 K respectively.

In order to minimize the number of refined parameters, only one Debye-Waller term for each type of atom was refined for the 300 K data (they were assumed to be equal to zero for the 4.2 K data). The magnetic Fe moments, the interstitial site occupancies, the crystal

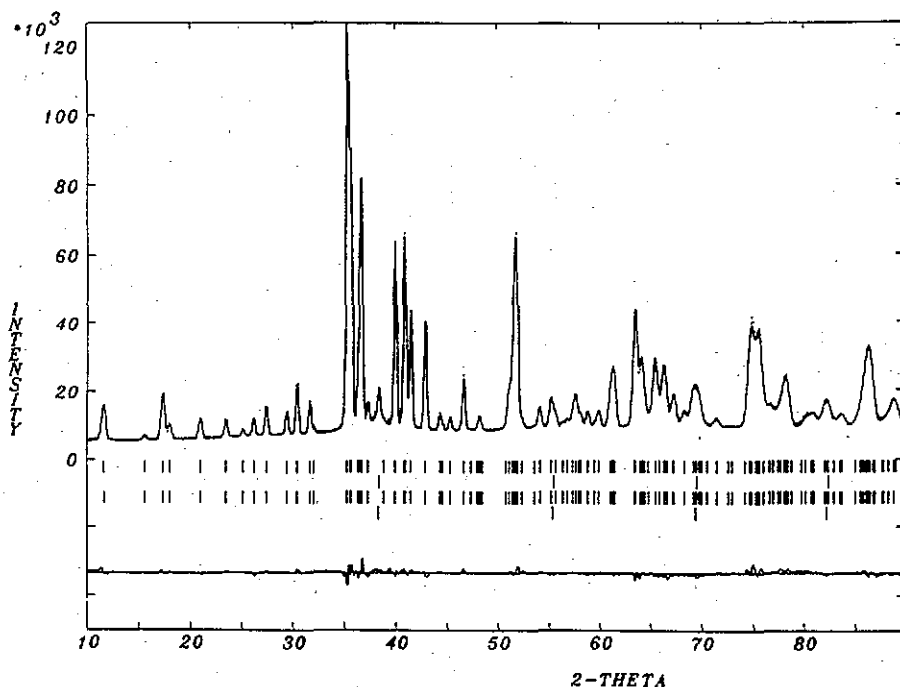


Figure 1. Neutron powder diffraction pattern of  $\text{Th}_2\text{Fe}_{17}\text{N}_3$  at room temperature. The points and the curve refer to the recorded pattern and the calculated fit respectively. A difference pattern is plotted in the lower part of the figure. The first and third sets of bars refer to the nuclear and magnetic diffraction peaks of  $\text{Th}_2\text{Fe}_{17}\text{N}_3$  respectively. The second set refers to  $\alpha\text{-Fe}$  as impurity.

Table 1. Lattice parameters and reliability factors from the  $\text{Th}_2\text{Fe}_{17}\text{X}_x$  crystal structure refinements. The agreement factors are defined as  $R_{\text{exp}} = [(N - P + C) / \sum_i w_i y_i^2]^{1/2}$  and  $R_p = \sum_i |y_i - y_{ci}| / \sum_i |y_i|$  where  $y_i$  and  $y_{ci}$  are the observed and calculated counts at the  $i$ th step of the pattern respectively.  $N - P + C$  is the number of degrees of freedom ( $N$  is the number of points in the pattern,  $P$  the number of refined parameters and  $C$  the number of constraint functions). The weights of the observations are calculated as  $w_i = 1/y_i$ . The magnetic reliability factor  $R_{\text{mag}}$  is defined as  $R_{\text{mag}} = \sum_i |l_k - l_{ck}| / \sum_k |l_k|$  where  $l_k$  and  $l_{ck}$  are the observed and calculated magnetic contributions to the integrated intensity at the  $k$ th reflection respectively.

Compound	$\lambda$ (Å)	$T$ (K)	$a$ (Å)	$c$ (Å)	$R_{\text{exp}}$ (%)	$R_{\text{mag}}$ (%)	$R_p$ (%)
$\text{Th}_2\text{Fe}_{17}\text{N}_3$	1.340	300	8.8020	12.737	0.82	4.87	2.64
$\text{Th}_2\text{Fe}_{17}\text{N}_3$	1.340	4	8.7653	12.691	1.17	4.88	6.12
$\text{Th}_2\text{Fe}_{17}\text{D}_5$	2.478	300	8.7116	12.624	0.65	5.62	2.51
$\text{Th}_2\text{Fe}_{17}\text{D}_5$	1.340	4	8.6820	12.560	0.99	5.09	5.83
$\text{Th}_2\text{Fe}_{17}\text{C}_{0.6}\text{H}_{4.4}$	2.495	300	8.7457	12.650	0.48	5.25	1.98
$\text{Th}_2\text{Fe}_{17}\text{C}_{0.6}\text{H}_{4.4}$	1.413	2	8.7510	12.643	0.35	5.45	1.70

$(x, y, z)$  and lattice parameters were simultaneously refined. The peak shape function used during the refinements was of the pseudo-Voigt type. In the case of  $\text{Th}_2\text{Fe}_{17}\text{C}_{0.6}\text{H}_{4.4}$ , the Fe magnetic moments were fixed at the values refined for  $\text{Th}_2\text{Fe}_{17}\text{D}_5$  in order to decrease the number of parameters.

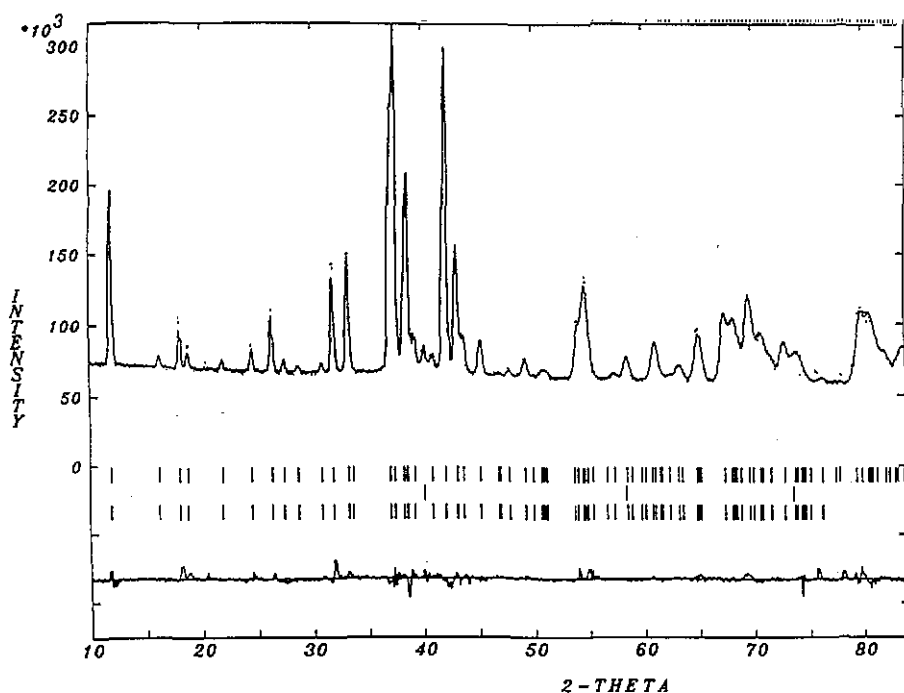


Figure 2. Neutron powder diffraction pattern of  $\text{Th}_2\text{Fe}_{17}\text{C}_{0.6}\text{H}_{4.4}$  at 4 K. The points and the curve refer to the recorded pattern and the calculated fit respectively. A difference pattern is plotted in the lower part of the figure. The first and third sets of bars refer to the nuclear and magnetic diffraction peaks of  $\text{Th}_2\text{Fe}_{17}\text{C}_{0.6}\text{H}_{4.4}$  respectively. The second set refers to  $\alpha$ -Fe as impurity.

### 3. Results and discussion

#### 3.1. Structural analysis

The lattice parameters for the three compounds as well as the reliability factors, are reported in table 1. With respect to  $\text{Th}_2\text{Fe}_{17}$  [11], the largest cell expansion is found for the nitride ( $x = 3$ ), the lattice being even larger than for  $\text{Th}_2\text{Fe}_{17}\text{C}_{0.6}\text{H}_4$ . The volume expansion per interstitial atom is  $6.3 \text{ \AA}^3/\text{N}$  in  $\text{Th}_2\text{Fe}_{17}\text{N}_3$ , and  $2.3 \text{ \AA}^3/\text{H}$  in  $\text{Th}_2\text{Fe}_{17}\text{D}_5$  and  $\text{Th}_2\text{Fe}_{17}\text{C}_{0.6}\text{H}_{4.4}$ . The expansion per H (D) atom is the same in  $\text{Th}_2\text{Fe}_{17}\text{C}_{0.6}\text{H}_{4.4}$  as in  $\text{Th}_2\text{Fe}_{17}\text{D}_5$ , in spite of the fact that the C atoms had already significantly increased the lattice prior to the H uptake. The volume expansion rate due to the C insertion is close to  $7 \text{ \AA}^3/\text{C}$ , in the concentration range 0.3–1.5 C/FU.

The interstitial atom concentrations refined for all these samples agree well with the upper limits previously reported [12]. Three N atoms per formula unit correspond to a complete filling of the octahedral sites—figure 3(a). Owing to the six too short inter-subsite distances and the corresponding repulsive forces, the filling of the tetrahedral sites is limited to  $\frac{1}{3}$  of the sites (2 H atoms/FU) [10, 12]. So the upper limit corresponds to a maximum of 5 H atoms/FU. The structure of  $\text{Th}_2\text{Fe}_{17}\text{D}_5$  is shown in figure 3(b). It is worth noting that the refined values for the amount of absorbed N or H (table 3: 2.96 N/FU, 4.96 D/FU and 4.4 H/FU) agree well with the values determined by the gravimetric method (3 N/FU, 4.9 D/FU and 4.2 H/FU). In the case of  $\text{Th}_2\text{Fe}_{17}\text{C}_{0.6}\text{H}_{4.4}$ , C is only accommodated

in the octahedral sites. In this case H fills both the remaining free octahedral sites and all the tetrahedral sites. Study of the interatomic distances leads to the conclusion that the N atom is strongly bonded to its nearest Fe neighbours. The bond distances  $d_{\text{N-Fe}_3} = 1.94 \text{ \AA}$  and  $d_{\text{N-Fe}_4} = 1.96 \text{ \AA}$  encountered in  $\text{Th}_2\text{Fe}_{17}\text{N}_3$  are very close to the shortest distances as measured in the Fe nitride  $\text{Fe}_4\text{N}$ . We have already noticed this feature in related  $\text{R}_2\text{Fe}_{17}$  nitrides [10].

Table 2. Room temperature magnetic moments ( $\mu_B$ ) of the Fe sites for  $\text{Th}_2\text{Fe}_{17}$ ,  $\text{Th}_2\text{Fe}_{17}\text{D}_5$ ,  $\text{Th}_2\text{Fe}_{17}\text{N}_3$ ,  $\text{Th}_2\text{Fe}_{17}\text{C}_{0.6}$  and  $\text{Th}_2\text{Fe}_{17}\text{C}_{0.6}\text{H}_{4.4}$ .

Site	$\text{Th}_2\text{Fe}_{17}$	$\text{Th}_2\text{Fe}_{17}\text{N}_3$	$\text{Th}_2\text{Fe}_{17}\text{D}_5$	$\text{Th}_2\text{Fe}_{17}\text{C}_{0.6}$ <sup>a</sup>	$\text{Th}_2\text{Fe}_{17}\text{C}_{0.6}\text{H}_{4.4}$
6c	—	3.06(0.9)	2.86(0.6)	1.20(09)	2.86
9d	—	2.76(09)	1.92(04)	1.20(09)	1.92
18f	—	1.94(08)	1.92(04)	1.20(09)	1.92
18h	—	1.81(0.8)	1.92(04)	1.20(09)	1.92

<sup>a</sup> From a previous study, see [11].

### 3.2. Magnetic analysis

Study of the local magnetic moments refined at low temperature for each of the Fe sites (table 4) reveals that N, C or H markedly increase the magnetization in comparison with pure  $\text{Th}_2\text{Fe}_{17}$ . All the magnetic moments are affected by the presence of the light elements. The moment ( $\sim 3\mu_B$ ) refined on the so-called dumbbell site (6c) is found to be the largest one of the structure (this is also a feature of the  $\text{Th}_2\text{Fe}_{17}$  alloy). The increase of magnetic moment due to C insertion seems to be less than the increase induced by N or D. This can be partly explained by the lower interstitial atom content in the carbide (0.6 C/FU) compared to the nitride (3 N/FU) or deuteride (5 H/FU). The magnetic moment observed on the 9d Fe site is also significantly increased by the interstitial element.

The strong variations of the magnetic moments found in various series of interstitial solid solutions of rare-earth compounds cannot be related to physical or chemical characteristics of the rare-earth element since we now find that it is also observed in Th compounds. Furthermore, such a moment variation has been observed also in other ternary iron-rich compounds such as  $\text{ThFe}_{11}\text{C}_x$  [13]. One of the parameters to account for the difference in size of the magnetic moments is probably the presence of p elements in the lattice [14]. Bulk magnetic measurements have confirmed that whatever the interstitial element, magnetization is higher in the ternaries than in  $\text{Th}_2\text{Fe}_{17}$ . This is observed both at 5 and 300 K as may be seen from table 5. Because the N content (3 instead of 2.6) in our case is higher than reported earlier [6, 7, 15], the saturation magnetization is also observed to be slightly higher than in the earlier investigations. The fully nitrated material exhibits by far the largest magnetization of all compounds studied. Such a tremendous magnetization increase with the insertion of a light element can be attributed to the increase of the unit cell volume and the concomitant interatomic Fe-Fe distances as was proposed earlier [16].

In spite of a higher content in interstitial atoms (5 as opposed to 3), the hydride exhibits a lower magnetization than  $\text{Th}_2\text{Fe}_{17}\text{N}_3$ . However, the magnetization is larger than in  $\text{Th}_2\text{Fe}_{17}\text{C}_{0.6}$  and  $\text{Th}_2\text{Fe}_{17}\text{C}_{1.2}$ . In the latter case,  $\text{Th}_2\text{Fe}_{17}\text{C}_x$ , one could expect that the higher the C content, the higher the magnetization, the magnetization of  $\text{Th}_2\text{Fe}_{17}\text{C}_{1.2}$  being closer to that of  $\text{Th}_2\text{Fe}_{17}\text{N}_3$  than  $\text{Th}_2\text{Fe}_{17}\text{C}_{0.6}$ .

Table 3. Structure determinations performed at low and room temperature on  $\text{Th}_2\text{Fe}_{17}\text{D}_5$ ,  $\text{Th}_2\text{Fe}_{17}\text{N}_3$ ,  $\text{Th}_2\text{Fe}_{17}\text{C}_{0.6}$  and  $\text{Th}_2\text{Fe}_{17}\text{C}_{0.6}\text{H}_{4.4}$ ;  $n$  are the relative occupancies. The Debye-Waller factors are given in  $\text{\AA}^2$ .

Atom	Site	$x$	$y$	$z$	$B$ ( $\text{\AA}^2$ )	$n$
$\text{Th}_2\text{Fe}_{17}\text{D}_5$ at 300 K						
Th	6c	0	0	0.3346(6)	0.4	0.1667
Fe(1)	6c	0	0	0.0995(4)	0.5	0.1667
Fe(2)	9d	0.5	0	0.5	0.5	0.25
Fe(3)	18f	0.284(3)	0	0	0.5	0.5
Fe(4)	18h	0.5047(2)	0.4953(2)	0.1572(3)	0.5	0.5
D(1)	9e	0.5	0	0	2.3	0.245(3)
D(2)	18g	0.8676(14)	0	0.5	2.3	0.168(3)
$\text{Th}_2\text{Fe}_{17}\text{D}_5$ at 4 K						
Th	6c	0	0	0.3351(5)	0	0.1667
Fe(1)	6c	0	0	0.0937(4)	0	0.1667
Fe(2)	9d	0.5	0	0.5	0	0.25
Fe(3)	18f	0.2833(3)	0	0	0	0.5
Fe(4)	18h	0.5031(2)	0.4969(2)	0.1572(3)	0	0.5
D(1)	9e	0.5	0	0	1.8	0.240(4)
D(2)	18g	0.8672(20)	0	0.5	1.8	0.149(6)
$\text{Th}_2\text{Fe}_{17}\text{N}_3$ at 300 K						
Th	6c	0	0	0.3426(3)	0.3	0.1667
Fe(1)	6c	0	0	0.0948	0.3	0.1667
Fe(2)	9d	0.5	0	0.5	0.3	0.25
Fe(3)	18f	0.2801(2)	0	0	0.3	0.5
Fe(4)	18h	0.5047(1)	0.4953(1)	0.1538(2)	0.3	0.5
N	9e	0.5	0	0	0.7	0.247(1)
$\text{Th}_2\text{Fe}_{17}\text{N}_3$ at 4 K						
Th	6c	0	0	0.3409(6)	0	0.1667
Fe(1)	6c	0	0	0.0956(4)	0	0.1667
Fe(2)	9d	0.5	0	0.5	0	0.25
Fe(3)	18f	0.2805(3)	0	0	0	0.5
Fe(4)	18h	0.5052(2)	0.4948(2)	0.1534(3)	0	0.5
N	9e	0.5	0	0	0.2	0.247
$\text{Th}_2\text{Fe}_{17}\text{C}_{0.6}\text{H}_{4.4}$ at 300 K						
Th	6c	0	0	0.3379(10)	0.5	0.1667
Fe(1)	6c	0	0	0.0979(7)	0.5	0.1667
Fe(2)	9d	0.5	0	0.5	0.5	0.25
Fe(3)	18f	0.2836(5)	0	0	0.5	0.5
Fe(4)	18h	0.5052(5)	0.4948(5)	0.1583(4)	0.5	0.5
C	9e	0.5	0	0	1	0.052
H(1)	9e	0.5	0	0	2.3	0.200
H(2)	18g	0.888(3)	0	0.5	2.3	0.156(6)
$\text{Th}_2\text{Fe}_{17}\text{C}_{0.6}\text{H}_{4.4}$ at 2 K						
Th	6c	0	0	0.3399(6)	0	0.1667
Fe(1)	6c	0	0	0.0943(4)	0	0.1667
Fe(2)	9d	0.5	0	0.5	0	0.25
Fe(3)	18f	0.2815(3)	0	0	0	0.5
Fe(4)	18h	0.5032(2)	0.4968(2)	0.1517(3)	0	0.5
C	9e	0.5	0	0	0.2	0.052
H(1)	9e	0.5	0	0	1.8	0.201
H(2)	18g	0.8760(33)	0	0.5	1.8	0.156(6)

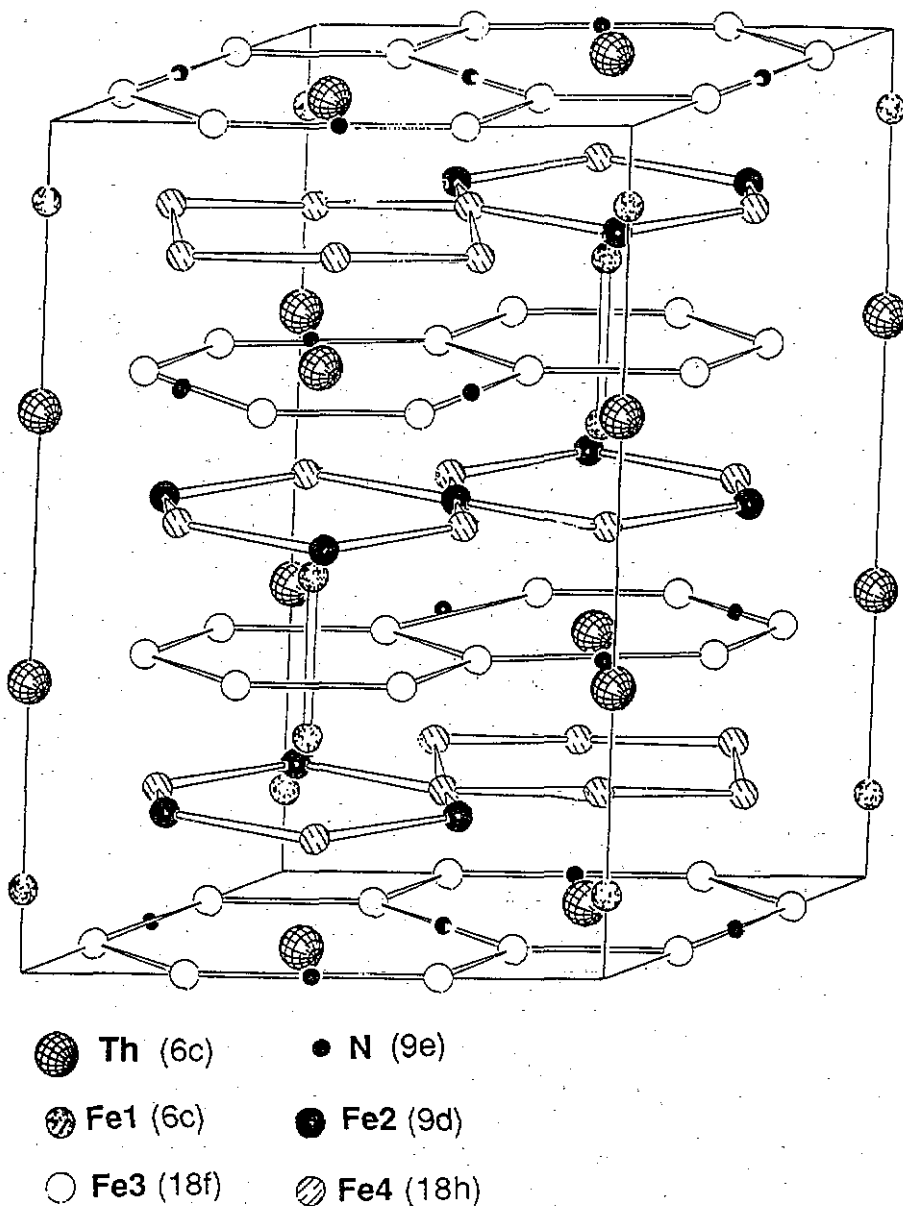
(a) **Th<sub>2</sub>Fe<sub>17</sub>N<sub>3</sub>**

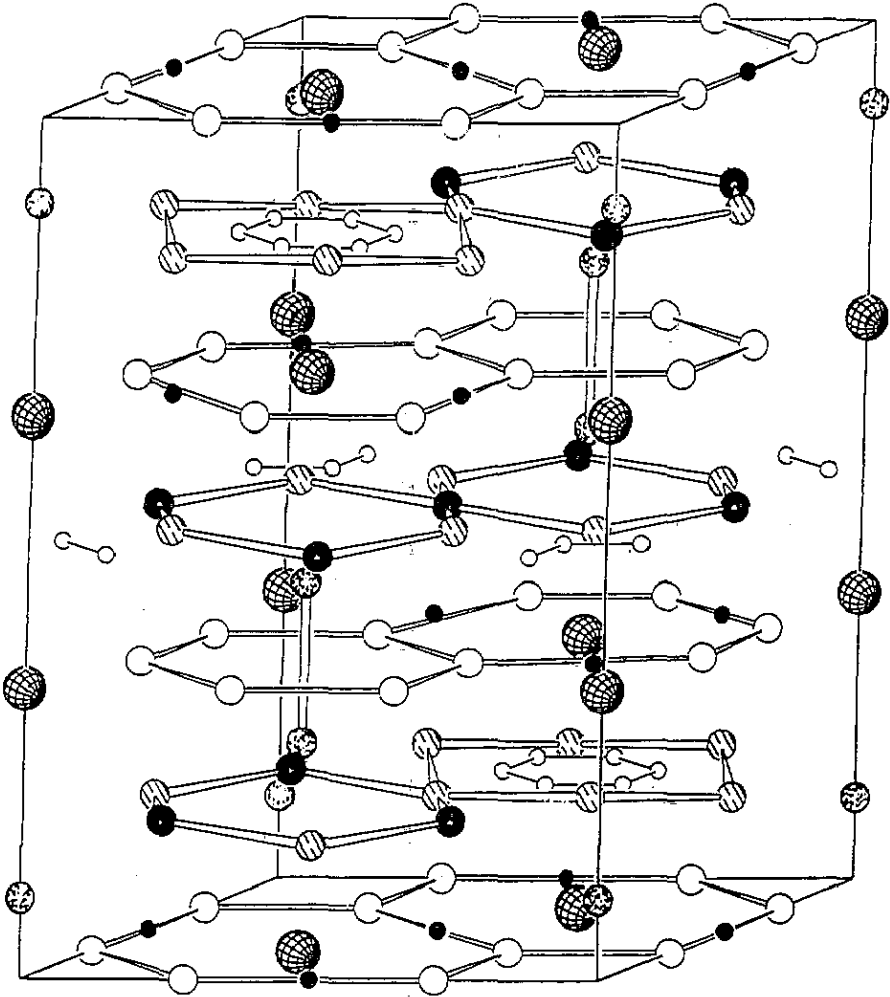
Figure 3. (a) Schematic representation of the  $Th_2Fe_{17}N_3$  structure. (b) Schematic representation of the  $Th_2Fe_{17}D_5$  structure.

### 3.3. Comparison of the $R_2Fe_{17}X_x$ series with the $R_2Fe_{14}B(C)$ series

We have shown that the bond length between iron and the p element (C or N) is very close to that encountered in the binary Fe carbides or nitrides. Unfortunately it is not possible to make a direct comparison between the 2-17-x and 2-14-1 compounds in terms of selected bond lengths and local magnetism since the C and N atoms are accommodated in octahedral



(b)

Th<sub>2</sub>Fe<sub>17</sub>D<sub>x</sub>

● Th (6c)

● Fe1 (6c)

● Fe2 (9d)

○ Fe3 (18f)

● Fe4 (18h)

● D1 (9e)

○ D2 (18g)

Figure 3. (Continued)

interstices in the 2-17-*x* compounds. By contrast, the C or B atoms are located in triangular prisms in the 2-14-1 compounds.

However, the different polyhedra correspond to the same coordination number (CN =

**Table 4.** Low-temperature magnetic moments ( $\mu_B$ ) of the Fe sites for  $\text{Th}_2\text{Fe}_{17}$ ,  $\text{Th}_2\text{Fe}_{17}\text{D}_5$ ,  $\text{Th}_2\text{Fe}_{17}\text{N}_3$ ,  $\text{Th}_2\text{Fe}_{17}\text{C}_{0.6}$  and  $\text{Th}_2\text{Fe}_{17}\text{C}_{0.6}\text{H}_{4.4}$ .

Site	$\text{Th}_2\text{Fe}_{17}$ <sup>a</sup>	$\text{Th}_2\text{Fe}_{17}\text{N}_3$	$\text{Th}_2\text{Fe}_{17}\text{D}_5$	$\text{Th}_2\text{Fe}_{17}\text{C}_{0.6}$ <sup>a</sup>	$\text{Th}_2\text{Fe}_{17}\text{C}_{0.6}\text{H}_{4.4}$
6c	2.81(12)	3.26(15)	3.41(13)	3.17(14)	3.20
9d	2.14(12)	2.74(15)	2.84(13)	2.11(13)	2.84
18f	1.83(9)	2.19(15)	2.30(09)	1.81(11)	2.30
18h	1.74(9)	2.15(11)	2.16(10)	1.76(11)	2.16

<sup>a</sup> From a previous study, see [11].

**Table 5.** Saturation magnetization (in  $\mu_B$ ) measured under 7 T, and Curie temperature in K.

Compound	Saturation magnetization		
	5 K	300 K	$T_C$
$\text{Th}_2\text{Fe}_{17}$	30.94	18.93	327
$\text{Th}_2\text{Fe}_{17}\text{C}_{0.6}$	32.60	24.32	396
$\text{Th}_2\text{Fe}_{17}\text{C}_{0.6}\text{H}_{4.2}$	36.32	31.64	501
$\text{Th}_2\text{Fe}_{17}\text{C}_{1.2}$	34.04	26.71	459
$\text{Th}_2\text{Fe}_{17}\text{D}_5$	35.75	31.62	471
$\text{Th}_2\text{Fe}_{17}\text{N}_3$	40.39	38.03	760

6) of the p element. Also the Fe-to-R ratios and the bond lengths are similar, so that one may expect that there is a certain similarity in the electronic properties. In fact, Herbst and Yelon [17] have pointed out that there exist analogous structural properties between  $\text{Nd}_2\text{Fe}_{14}\text{B}$  and  $\text{Nd}_2\text{Fe}_{17}$ . They observed that the  $j_2$  site in the 2-14-1 structure and the 6c site in the 2-17 structure (dumbbell site) are crystallographic as well as magnetic cognates. Within the corresponding type of structure, each of these sites exhibits the largest number of nearest Fe neighbours, and the largest magnetic moment ( $\sim 3\mu_B$ ). The lowest magnetic moment measured in the series  $\text{Th}_2\text{Fe}_{17}\text{X}_x$  ( $X = \text{H}, \text{C}, \text{N}$ ) belongs to the Fe atoms (18h) directly bonded to the interstitial element as may be seen from tables 2 and 3. The bond length between the Fe atoms at the 18h and the N atom is equal to 1.96 Å. Such a short Fe-p-element bond length has been reported previously in  $\text{R}_2\text{Fe}_{14}\text{B}$  [18], where it was also accompanied by the lowest Fe magnetic moment.

In the two series considered a wide range of intermediate bond lengths as well as intermediate magnetic moments exist; in a rough approximation one would expect that there would be a correlation between the CN, the number and the length of the Fe-non-metal bonds on the one hand and the local magnetic polarization on the other hand. Unfortunately, a comparison cannot yet be made because the magnetic moments reported in the literature [19-21] differ strongly from one study to the other. Also, more accurate crystal structure determinations would be needed. This question will be addressed in a forthcoming paper [14].

#### 4. Conclusion

We have determined the crystal structure and the magnetic structures of the interstitial compounds  $\text{Th}_2\text{Fe}_{17}\text{N}_3$ ,  $\text{Th}_2\text{Fe}_{17}\text{D}_5$  and  $\text{Th}_2\text{Fe}_{17}\text{C}_{0.6}\text{H}_{4.4}$ . The elements N and C occupy only the octahedral 9e sites whereas H can be found in both the octahedral (9e) and tetrahedral (18g) sites. In the case of  $\text{Th}_2\text{Fe}_{17}\text{C}_{0.6}\text{H}_{4.4}$ , the H atoms fill the remaining octahedral sites, already partly occupied by C, and the tetrahedral sites. The p elements are found to be

strongly bonded to the surrounding Fe atoms, with interatomic distances falling into the same range as found in the binary Fe nitrides or carbides. The Curie temperatures as well as the magnetizations are dramatically enhanced by insertion of the light elements.

The upper concentrations of the interstitial elements in  $\text{Th}_2\text{Fe}_{17}$  (3 N atoms per formula unit, 5 H atoms per formula unit), are in concord with observations made on rare-earth compounds  $\text{R}_2\text{Fe}_{17}\text{X}_x$  [3, 12, 22]. The analogy in behaviour between  $\text{Th}_2\text{Fe}_{17}$  and  $\text{R}_2\text{Fe}_{17}$  extends also to the comparatively large Fe magnetic moment observed on the dumbbell site and the large variety in the other moments and their dependence on the CN and bond lengths of the corresponding sites. Of particular interest is the result that the Fe moment enhancement relative to  $\text{Th}_2\text{Fe}_{17}$  is larger in  $\text{Th}_2\text{Fe}_{17}\text{H}_5$  than in  $\text{Th}_2\text{Fe}_{17}\text{N}_3$ , while the opposite holds for the corresponding Curie temperatures. These results show that the effect of the volume increase and Fe atom bonding to the interstitial atoms have different influences on moment site and ordering temperature.

Finally the  $\text{R}_2\text{Fe}_{17}\text{N}(\text{C})_3$  series (R = Th or rare-earth metal) has been compared to the  $\text{R}_2\text{Fe}_{14}\text{B}(\text{C})$  series. Although of different crystal structure, the two types of compound show some similarities in the atom environments, as well as in the corresponding local magnetic moments.

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