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Neutron diffraction study on the deuterium site occupation and magnetic structure of the $Nd_2(Fe,Ga)_{14}BD_y$ compounds

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Abstract

Synthesis and characterization of $Nd_2Fe_{14-x}Ga_xBD_y$ compounds are presented for $x=1$, 1.8 and $y=0$ to 4. The influence of the deuteration has been studied both on the structural and magnetic properties. Our present investigation has been performed at both 4 and 300 K by means of high-resolution powder neutron diffraction. A decrease of the maximum quantity of deuterium inserted upon Ga substitution is evidenced. The location of the D atoms within the tetragonal $Nd_2Fe_{14}B$ structure for the $Nd_2Fe_{13}GaBD_{3.7}$ and $Nd_2Fe_{12.2}Ga_{1.8}BD_{3.2}$ compounds is presented. The D insertion was revealed to be possible in four tetrahedral D sites. A blocking of the D ($16k_2$) site in the Ga-containing samples is demonstrated. The evolution of the occupancies of the different sites is linked with the modification of the distances and of the nature of the nearest neighbors. An increase of the Curie temperature upon D insertion is measured but the magnitude of this enhancement is less pronounced in comparison with the effect of the D insertion in the pure $Nd_2Fe_{14}B$. The evolution of the magnetic moments carried by each atom shows an increase of the mean Fe moment upon D insertion. Finally, the saturation magnetization is found to increase upon D insertion but this rise is not directly related to the quantity of D inserted.

Keywords: $Nd_2Fe_{14}B$; Hydrides; Powder neutron diffraction; Magnetic properties

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1. Introduction

Since its discovery in 1984 [1,2], the $Nd_2Fe_{14}B$ phase has been widely studied because of its high performances as a material for permanent magnet purposes [3]. Meanwhile, a relatively low Curie temperature (T_C) restricts the thermal applications of permanent magnets based on the $Nd_2Fe_{14}B$ compound. The substitution of a small amount of gallium for iron is possible and induces a modification of the magnetic properties of the $Nd_2Fe_{14}B$ phases. In particular, an interesting increase of about 7% of the T_C is observed upon Ga for Fe substitution.

The $Nd_2Fe_{14}B$ compound is known to absorb a significant amount of hydrogen (H) or deuterium (D) [4,5] forming stable hydrides (deuterides) that still preserve the tetragonal $Nd_2Fe_{14}B$ crystal structure. Deuterium insertion results in an expansion of the unit cell volume but also in a modification of the magnetic properties such as the Curie temperature, the saturation magnetization (M_s), the spin reorientation temperature (T_{sr}) and the magnetocrystalline anisotropy [6].

The D absorption induces a decrepitation in small grains of the pure starting ingots. Among the different manufacturing routes of $Nd_2Fe_{14}B$-type permanent magnets, two processes are based on hydrogen absorption: the hydrogen decrepitation (H.D.) [7] and the hydrogenation disproportionation, desorption and recombination (H.D.D.R.) [8]. The performances of these processes were found to be improved in the case of the Ga-containing $Nd_2Fe_{14}B$ phases [9,10].

Neutron diffraction studies have demonstrated that deuterium occupies selected tetrahedral interstitial sites of the $Nd_2Fe_{14}B$ structure. The insertion scheme of deuterium within the structure has evidenced serious differences in the maximum quantity of deuterium inserted in the four possible sites. This behavior was linked to the size but also to the chemical nature of the nearest neighbors of each site [11].

The Ga for Fe substitution exhibits a preferential substitution scheme favoring the 4*c* site of the structure [12]. Consequently, an evolution of the maximum quantity of deuterium inserted in the $Nd_2Fe_{14-x}Ga_xB$ is expected.

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The influence on the magnetic properties of the deuterium insertion in the Ga-containing sample is also likely to be different to that observed on the pure $Nd_2Fe_{14}B$ one.

We report on the evolution of the maximum quantity of deuterium uptake in the $Nd_2Fe_{14-x}Ga_xB$ compounds and its effects on the crystal structure. Neutron diffraction studies have been performed on the fully deuterated samples and the location of deuterium in the $Nd_2Fe_{14-x}Ga_xB$ crystal structure is addressed. We also discuss the evolution of the atomic magnetic moments and of the macroscopic magnetic properties of the $Nd_2Fe_{14-x}Ga_xB$ compounds upon deuterium insertion.

2. Experimental details

The neutron diffraction experiments were performed at the Institute Laüe Langevin (I.L.L.) in Grenoble France using the high-resolution two-axis diffractometer D2B whose description is given in the I.L.L. web site [13]. The diffraction patterns have been recorded for a 2θ range of 160°, with step size of 0.05°. For each compound, the measurements were carried out at both 4 and 300 K using a wavelength (λ) equal to 1.59 Å. The samples were synthesized using ^{11}B rather than ^{10}B in order to lower the neutron absorption cross section. Deuterium was preferred to hydrogen in order to avoid the incoherent scattering of H.

The polycrystalline samples were prepared by melting the starting materials (purity of 99.9% at least) in a high frequency furnace in an argon atmosphere. Small pieces of the ingots were then wrapped in a Ta foil, sealed in a silica tube under vacuum and annealed at 1173 K for a week for better homogeneity.

The lattice parameters of each compound were refined from high resolution X-ray diffractograms recorded on a Guinier-type focusing camera operating with the iron K α_1 wavelength ($\lambda = 1.9373$ Å).

Deuterations were performed in a dedicated stainless steel autoclave under a D_2 gas pressure of about 2 MPa. The D insertion was initiated by at least three thermal activation cycles at 473 K leading to fully deuterated compounds. The quantity of deuterium inserted in the alloys was determined by gravimetric method. The precision of the deuterium uptake determination has been estimated to be equal to 0.1 deuterium atom per formula unit (D/f.u.).

The T_C was measured using a Faraday-type balance with a heating and cooling rate of 5 K per min. The magnetization (M_s) measurements were performed using the extraction method in a continuous field up to 7 T.

3. Results and discussion

3.1. Crystal structure

The solubility limit of Ga in the $Nd_2Fe_{14}B$ phases was determined to be equal to 1.8 Ga atom per formula unit. We have synthesized the fully deuterated samples of both $Nd_2Fe_{13}GaB$ and $Nd_2Fe_{12.2}Ga_{1.8}B$. The maximum quantity of D uptake was found to decrease significantly (Table 1) when the Ga concentration increases. Only 3.2 D atoms per formula unit can be inserted in $Nd_2Fe_{12.2}Ga_{1.8}B$ whereas the maximum quantity of D taken up in $Nd_2Fe_{14}B$ is equal to 5 D/f.u. [14]. The decrease of the maximum quantity of D inserted is not a consequence of a cell contraction because the unit cell volume is found to increase when the Ga concentration increases. It is to be noticed that this unit cell volume expansion is not isotropic: as shown in Table 1, the c/a parameter increases upon Ga for Fe substitution evidencing a more pronounced increase of the c lattice parameter. The volume increase of the unit cell per D atom ($\Delta V/D$) inserted depends on the Ga concentration. As shown in Table 1, the volume expansion is equal to 2.5 Å^3 per D atom inserted in $Nd_2Fe_{13}GaB$ whereas it is only 2.1 Å^3 per D atom inserted for $Nd_2Fe_{12.2}Ga_{1.8}B$. This behavior is a singularity of the Ga-containing samples because Isnard et al. [11] have evidenced a decrease of the $\Delta V/D$ factor when the quantity of D inserted increases in the pure $Nd_2Fe_{14}B$ phases.

Previous studies have also evidenced a decrease of the maximum quantity of D taken up when replacing iron by another element such as silicon [14] or cobalt [15]. In these cases, the Si or Co for Fe substitution induces a decrease of the unit cell volume. Such a unit cell volume decrease is

Table 1
Lattice parameters, Curie temperatures and saturation magnetizations of $Nd_2Fe_{14-x}Ga_xBD_y$ phases

	$Nd_2Fe_{14}B$	$Nd_2Fe_{13}GaB$	$Nd_2Fe_{12.2}Ga_{1.8}B$	$Nd_2Fe_{13}GaBD_{3.7}$	$Nd_2Fe_{12.2}Ga_{1.8}BD_{3.2}$
a (Å)	8.808 (1)	8.794 (1)	8.803 (1)	8.936 (2)	8.908 (2)
c (Å)	12.207 (2)	12.301 (2)	12.329 (3)	12.375 (4)	12.384 (3)
c/a	1.386	1.398	1.401	1.385	1.390
V (Å^3)	947.0	951.2	955.4	988.2	982.7
$\Delta V/D$ (Å^3/D)	–	–	–	2.5	2.1
T_c (K)	585 (3)	627 (3)	624 (3)	680 (3)	664 (3)
M_s (μ_B/f.u.)					
4 K	35.0 (1)	30.7 (1)	23.7 (1)	31.8 (1)	25.7 (1)
300 K	31.9 (1)	26.4 (1)	19.2 (1)	28.3 (1)	23.8 (1)

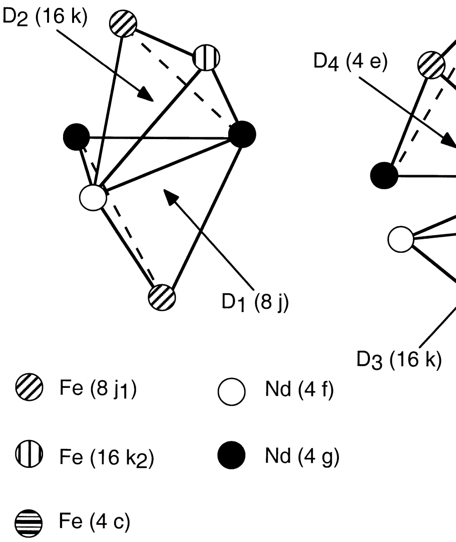

Fig. 1. Description of the four possible deuterium interstitial sites in the $Nd_2Fe_{14}B$ structure.

not observed in the case of the gallium for iron substitution. One can propose that the observed decrease of the maximum quantity of D inserted is linked to the chemical nature of the substitution element (Ga) but also to the preferential substitution scheme of Ga. In this aim, a precise localization of the D atoms within the crystal structure was required.

A description of the D interstitial sites is given in Fig. 1. We will adopt in this article the description of the atomic positions first used by Herbst et al. [16]. We have recorded the powder neutron diffraction patterns of the $Nd_2Fe_{12}GaBD_{3.7}$ and $Nd_2Fe_{12.2}Ga_{1.8}BD_{3.2}$ samples at both 4 and 300 K. An example of the obtained diffractograms is given in Fig. 2. The data were analyzed using the Rietveld structure refinement program FULLPROF [17]. The atomic coordinates of each atom as well as the reliability factors of the refinements are listed in Table 2. An excellent agreement is found for the Ga occupancies of the different sites between the starting alloys and the deuterides. No major changes are found in the atomic coordinates of the deuterium-containing samples and the pure $Nd_2Fe_{14-x}Ga_xB$ phases. Fig. 3 gives the evolution of the D occupancies in the four different D sites. It is to be noticed that deuterium is found in each possible interstitial site. On the one hand, the atomic coordinates of the D sites are observed to be independent of the Ga content. On the other hand, serious modifications are observed in the D occupancies as a function of the Ga concentration. It is to be remembered that in the deuterium absorbing compounds formed or substituted by p-electron elements such as boron, aluminum, silicon or gallium, the s-like character

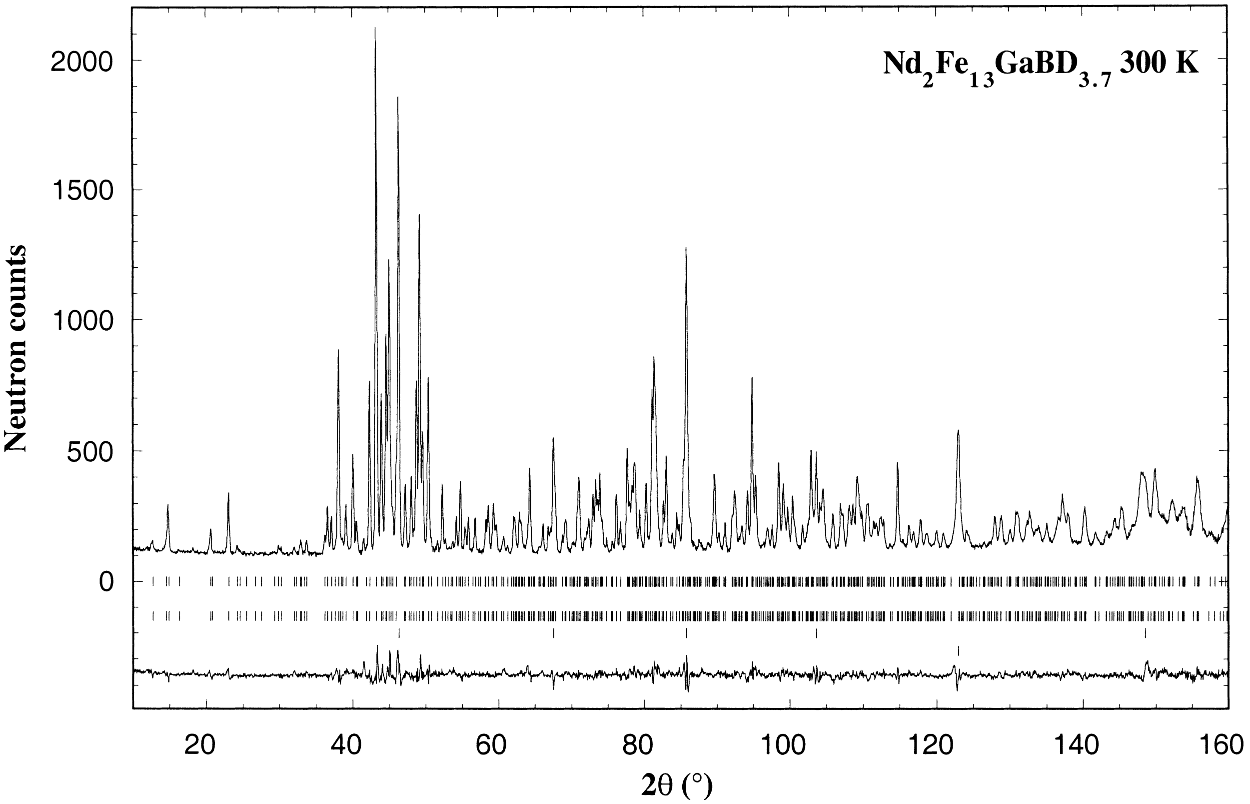

Fig. 2. Neutron diffraction pattern of $Nd_2Fe_{13}GaBD_{3.7}$ obtained at 300 K on the D2B diffractometer. The rows of vertical bars refer to the nuclear and magnetic contribution to the diffraction pattern. The last row stands for the small amount of α-iron impurity. The difference between the experimental data and the calculated fit is plotted on the bottom of the figure.

Table 2
Structural parameters and magnetic moments obtained from neutron diffraction refinement of $Nd_2Fe_{14-x}Ga_xBD_y$ at 4 and 300 K

			$Nd_2Fe_{13}GaBD_{3.7}$		$Nd_2Fe_{12.2}Ga_{1.8}BD_{3.2}$	
			4 K	300 K	4 K	300 K
Atomic positions						
Nd	4*f*	*x*	0.2791 (3)	0.2797 (3)	0.2794 (5)	0.2782 (5)
Nd	4*g*	*x*	0.1509 (3)	0.1509 (3)	0.1507 (6)	0.1507 (6)
Fe	4*e*	*z*	0.3822 (3)	0.3831 (3)	0.3841 (5)	0.3838 (6)
Fe	$8j_1$	*x*	0.3999 (2)	0.4001 (2)	0.4011 (4)	0.4001 (4)
Fe	$8j_1$	*z*	0.2981 (2)	0.2978 (2)	0.2997 (3)	0.2987 (3)
Fe	$8j_2$	*x*	0.1824 (2)	0.1821 (2)	0.1819 (3)	0.1828 (2)
Fe	$8j_2$	*z*	0.2543 (2)	0.2545 (2)	0.2535 (4)	0.2539 (4)
Fe	$16k_1$	*x*	0.7290 (2)	0.7286 (2)	0.7305 (3)	0.7301 (3)
Fe	$16k_1$	*y*	0.0677 (2)	0.0676 (2)	0.0676 (3)	0.0676 (4)
Fe	$16k_1$	*z*	0.3669 (1)	0.3675 (1)	0.3645 (2)	0.3664 (3)
Fe	$16k_2$	*x*	0.4639 (1)	0.4638 (2)	0.4633 (3)	0.4638 (3)
Fe	$16k_2$	*y*	0.1352 (2)	0.1358 (2)	0.1347 (3)	0.1361 (3)
Fe	$16k_2$	*z*	0.3224 (1)	0.3269 (1)	0.3221 (2)	0.3224 (3)
D	4*e*	*z*	0.615 (1)	0.615 (1)	0.620 (5)	0.627 (5)
D	8*j*	*x*	0.400 (4)	0.402 (4)	0.403 (4)	0.395 (4)
D	8*j*	*z*	0.559 (3)	0.571 (3)	0.558 (3)	0.578 (3)
D	$16k_1$	*x*	0.441 (1)	0.440 (1)	0.443 (1)	0.442 (1)
D	$16k_1$	*y*	0.281 (1)	0.280 (1)	0.286 (1)	0.286 (1)
D	$16k_1$	*z*	0.595 (1)	0.596 (1)	0.596 (1)	0.596 (1)
D	$16k_2$	*x*	0.466 (2)	0.471 (2)	0.497 (5)	0.478 (4)
D	$16k_2$	*y*	0.175 (2)	0.173 (2)	0.160 (5)	0.164 (5)
D	$16k_2$	*z*	0.538 (1)	0.544 (1)	0.530 (3)	0.546 (3)
B	4*g*	*x*	0.3735	0.3735	0.3735	0.3735
Magnetic moments (μ_B)						
Nd	4*f*		2.3 (1)	1.6 (2)	1.4 (2)	1.1 (2)
Nd	4*g*		2.5 (1)	1.6 (2)	1.6 (1)	1.2 (2)
Fe	4*c*		2.5 (2)	2.4 (2)	2.1 (2)	1.9 (2)
Fe	4*e*		2.3 (2)	2.1 (2)	2.2 (2)	2.2 (3)
Fe	$8j_1$		2.8 (2)	2.5 (2)	2.4 (2)	2.4 (1)
Fe	$8j_2$		3.0 (1)	2.9 (1)	2.4 (2)	2.9 (3)
Fe	$16k_1$		3.0 (1)	2.6 (1)	3.1 (1)	2.9 (2)
Fe	$16k_2$		2.9 (1)	2.6 (2)	3.0 (1)	2.7 (2)
⟨Fe⟩			2.7 (1)	2.6 (1)	2.8 (1)	2.8 (2)
Reliability factors (%)						
R_{wp}			9.5	10.2	6.8	6.3
R_{exp}			4.5	6.0	5.5	3.1
R_{bragg}			4.5	4.0	6.6	6.7
R_{mag}			6.4	5.5	11.5	9.8
χ^2			4.5	2.9	2.6	4.0

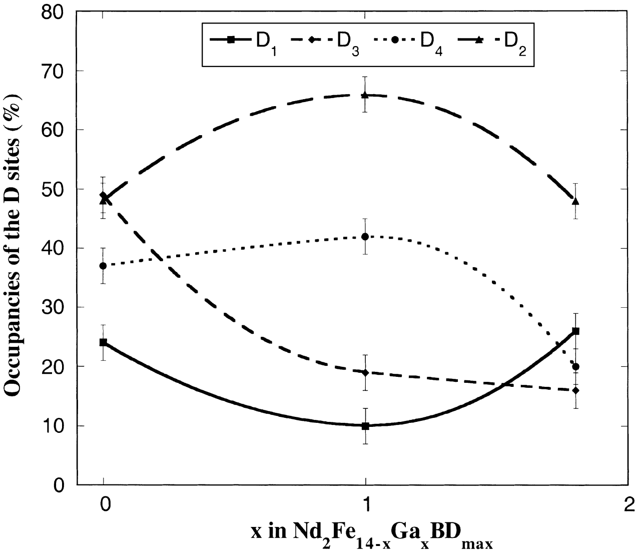

Fig. 3. Evolution of the occupancy of the D interstitial sites upon Ga for Fe substitution in the $Nd_2Fe_{14-x}Ga_xBD_y$ compounds.

atoms do not bond directly with the former elements [18]. Relying on the work of Rundquist et al. [18], one can expect that the Ga atoms tend to block the filling of the neighboring interstitial sites by D atoms. Since the Ga for Fe substitution occurs preferentially on some peculiar iron sites, the influence on the D filling should differ significantly from one interstitial site to the other.

A dramatic decrease of the D quantity inserted in the D_3 sites is exhibited in the Ga-containing samples. As reported in Table 3, the nearest neighbors of the D_3 site are the Nd (4*f*), Nd (4*g*), Fe (4*c*) and Fe ($16k_2$) atoms. The calculated inter-atomic distances evidenced an increase of the D_3–Nd (4*g*) and D_3–Nd (4*f*) distances and a decrease of the D_3–Fe (4*c*) and D_3–Fe ($16k_2$) ones. We have also to keep in mind the Ga for Fe substitution scheme has demonstrated a preference of Ga for the Fe (4*c*) sites and that this site has already a Ga occupancy of 50% in $Nd_2Fe_{13}GaB$. That is to say that the D_3 site environment is rich in Ga atoms in comparison with the other D sites. Consequently, the low occupancy of this D_3 site is due to the large number of Ga near neighbors exhibited by this site.

A two-step behavior is observed for the occupancies of the D_4 site. Firstly, the quantity of D inserted in these sites increases when the Ga concentration goes up from $x=0$ to $x=1$. Then the D occupancy is decreasing for $x=1.8$. The D_4 site has been evidenced to be the last one to be filled in the non-Ga-containing sample [11]. The reason for this is the too small size of this site that makes it hard to be filled by D atoms. This site environment is constituted by two Nd (4*f*) and two Fe ($8j_1$) atoms. The quantity of D inserted in this D_4 site in the $Nd_2Fe_{13}GaBD_{3.7}$ compound is slightly increasing in comparison to what happens in $Nd_2Fe_{14}BD_4$. Only about 10% of Ga atoms were found in the Fe ($8j_1$) in $Nd_2Fe_{13}GaB$. Consequently, the chemical nature of the atoms constituting the D_4 site environment is not significantly changed by the Ga for Fe substitution. Thus, the observed increase of the occupancy of the D_4 site is linked to the observed increase of the unit cell volume upon Ga substitution. In the case of the $Nd_2Fe_{12.2}Ga_{1.8}BD_{3.2}$ compound, the quantity of Ga substituted in the Fe ($8j_1$) has significantly increased. As a result, the number of Ga atoms being nearest neighbors of the D_4 site has risen. This feature induces the decrease of the maximum quantity of D uptake by the D_4 site in $Nd_2Fe_{12.2}Ga_{1.8}BD_{3.2}$.

Such an explanation is corroborated by the case of the

Table 3
Deuterium–metal inter-atomic distances in the $Nd_2Fe_{14-x}Ga_xBD_y$ structures

Distance (Å)	$Nd_2Fe_{14}BD_4$	$Nd_2Fe_{13}GaBD_{3.7}$	$Nd_2Fe_{14}BD_3$	$Nd_2Fe_{12.2}Ga_{1.8}BD_{3.2}$
D_1–Nd (4*g*)	2.41	2.45	2.38	2.50
D_1–Nd (4*f*)	2.44	2.48	2.36	2.39
D_1–Fe (8j_1)	1.65	1.58	1.63	1.53
D_2–Nd (4*g*)	2.27	2.31	2.25	2.27
D_2–Nd (4*f*)	2.31	2.35	2.32	2.36
D_2–Fe (8j_1)	1.72	1.74	1.64	1.70
D_2–Fe (16k_2)	1.70	1.66	1.71	1.69
D_3–Nd (4*g*)	2.24	2.30	2.24	2.32
D_3–Nd (4*f*)	2.29	2.34	2.25	2.41
D_3–Fe (4*c*)	1.69	1.67	1.67	1.58
D_3–Fe (16k_2)	1.75	1.69	1.74	1.66
D_4–Nd (4*f*)	2.34	2.37	2.29	2.47
D_4–Fe (8j_1)	1.65	1.66	1.68	1.56

D_2 interstitial site. The evolutions upon Ga for Fe substitution of the occupancies of the D_2 and D_4 sites are roughly the same. Table 3 reminds us that the nearest neighbors of the D_2 site are one Nd (4*f*), one Nd (4*g*), one Fe (8j_1) and one Fe (16k_2) atom. The number of Ga atoms in the neighborhood of this site starts to be significant for $Nd_2Fe_{12.2}Ga_{1.8}BD_{3.2}$. As in the case of the D_4 site, the observed two-step behavior is the result of a competition between the increase of the site's size due to the unit cell volume expansion and the increase of the number of Ga atoms in the site environment. The two effects being opposite: the expansion of the unit cell volume favoring a higher D content whereas the presence of Ga atoms tends to block the D insertion.

The D_1 site is less sensitive to the Ga for Fe substitution because the environment of this site is constituted by three Nd atoms and only one Fe (8j_1) atom. The filling scheme of D in the $Nd_2Fe_{14}BD_y$ has evidenced a decrease of the quantity of D inserted in this site between $y=3$ and $y=4$ [11]. The decrease of the quantity of D inserted in D_1 was linked to the increase of filling of the D_2 site since these two tetrahedral sites are sharing an edge (Fig. 1). Consequently, the D insertion in the D_2 site reduces significantly the D_1 site size. Since the filling of the D_2 site is also increasing when the maximum quantity of D inserted in the Ga-containing increases, this excludes even more the filling of some of the neighboring D_1 site. We can conclude that the evolution of the filling of the D_1 site upon Ga for Fe substitution is induced by the filling of the D_2 site.

3.2. Magnetic properties

The insertion of deuterium is also known to modify the magnetic properties of the $Nd_2Fe_{14}B$ phases. Néel [19] has demonstrated that the exchange interactions between transition metal atoms are very sensitive to the inter-atomic distances. The crystal structure modifications induced by the D insertion are expected to change the T_C via a modification of the exchange interactions. As reported in Table 1, the deuteration of the $Nd_2Fe_{14-x}Ga_xB$ compounds induces an increase of the T_C. This increase depends on the quantity of D inserted in the starting alloy. The increase of T_C in the fully deuterated compounds is equal to 53 and 40 K for $Nd_2Fe_{13}GaB$ and $Nd_2Fe_{12.2}Ga_{1.8}B$, respectively. It is to be noticed that for the $Nd_2Fe_{14}B$ pure phase the observed increase was estimated to 18 K per D atom inserted [20]. In rare-earth (R)–transition metal (M) compounds, three types of exchange interactions occur: M–M, R–M, R–R. It is well established that the M–M interaction dominates and determines the magnitude of the T_C [21]. Consequently, the increase of the T_C upon D insertion can be linked to the evolution of the Fe–Fe inter-atomic distances. In Table 4, we have reported the shorter Fe–Fe inter-atomic distances in the $Nd_2Fe_{14-x}Ga_xBD_y$ compounds. The increase of these shortest distances upon Ga for Fe substitution induces the increase of the exchange interactions and of the T_C [22,23]. The effect of the D insertion is an additive enhancement of these distances in both $Nd_2Fe_{13}GaBD_{3.7}$ and $Nd_2Fe_{12.2}Ga_{1.8}BD_{3.2}$. The more significant Fe–Fe inter-atomic distance increase upon D insertion occurs between the Fe (8j_1) and Fe (16k_2) i.e. this distance goes from 2.3 Å for $Nd_2Fe_{13}GaB$ to 2.45 Å for $Nd_2Fe_{13}GaBD_{3.7}$. The Fe (8j_1)–Fe (8j_1) is also significantly increased upon D insertion as reported in Table 4. This feature explains the increase of the T_C upon D insertion in the Ga-containing compounds. The increase of the shortest Fe–Fe inter-atomic distances upon D insertion is roughly the same for both Ga concentrations. One can expect that the increase of T_C should be the same. In fact, we have observed that the increase of T_C is superior by 13 K in the case of the D insertion in $Nd_2Fe_{13}GaB$ to that measured for $Nd_2Fe_{12.2}Ga_{1.8}B$. We have to keep in mind that the number of interaction exchanges involving only Fe atoms is decreasing upon Ga substitution. An increasing number of these distances are connecting gallium atoms to

Table 4
Shortest Fe–Fe inter-atomic distances in the $Nd_2Fe_{14-x}Ga_xBD_y$ structures

Distance (Å)	$Nd_2Fe_{14}BD_y$		$Nd_2Fe_{13}GaBD_y$		$Nd_2Fe_{12.2}Ga_{1.8}BD_y$	
	$y=0$	$y=4$	$y=0$	$y=3.7$	$y=0$	$y=3.2$
Fe ($16k_1$)–Fe ($16k_2$)	2.46	2.48	2.46	2.50	2.47	2.50
Fe ($4e$)–Fe ($16k_1$)	2.50	2.50	2.49	2.51	2.49	2.49
Fe ($16k_2$)–Fe ($4c$)	2.49	2.52	2.51	2.53	2.52	2.53
Fe ($8j_1$)–Fe ($16k_2$)	2.39	2.43	2.39	2.45	2.39	2.44
Fe ($8j_1$)–Fe ($8j_1$)	2.44	2.50	2.44	2.52	2.47	2.52
Fe ($8j_1$)–Fe ($4e$)	2.52	2.50	2.55	2.57	2.55	2.58

iron atoms but since Ga is non-magnetic, there is no exchange interactions between Ga and its near neighbors. Consequently, the increase in the inter-atomic distances upon D insertion is less efficient to increase the overall interaction exchange because more Fe atoms have been replaced by Ga ones. Therefore, the rise of T_C upon D insertion is less efficient for the higher Ga concentration.

The saturation magnetization and the magnetic moments carried by each atom are also sensitive to the D insertion. Fig. 4 gives the magnetization versus applied field at 4 and 300 K for the deuterated samples. The M_s obtained by extrapolation to zero field are listed in Table 1. The D insertion induces an increase of the M_s at both 4 and 300 K in the two Ga-containing samples.

Firstly, the decrease of M_s in the deuterated compounds when the temperature increases is mainly due to the dramatic decrease of the magnetic moments carried by the Nd atoms. For $Nd_2Fe_{13}GaBD_{3.7}$, the mean magnetic moment carried by the Nd atoms is equal to 2.5 μ_B at 4 K against 1.6 μ_B at 300 K. On the contrary, the mean Fe magnetic moment is almost unchanged between 4 and 300 K if we keep in mind that the error bars on the measured magnetic moments are equal to 0.1 μ_B (Table 2).

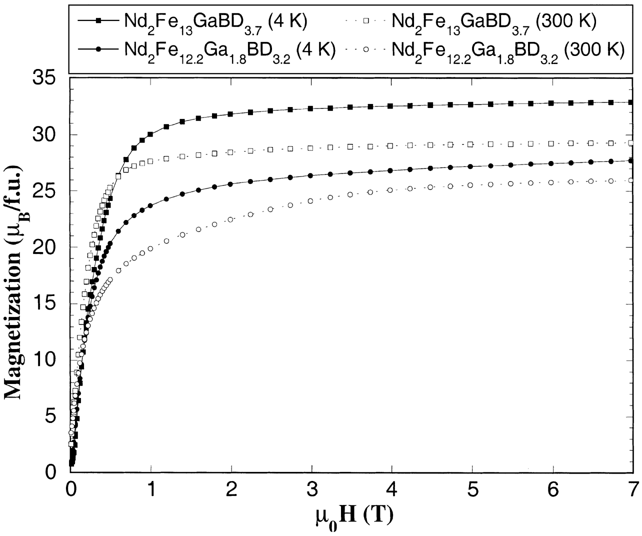

Fig. 4. Isothermal magnetization curves recorded at 4 K (continued line and full symbols) and 300 K (dashed line and open symbols) for $Nd_2Fe_{13}GaBD_{3.7}$ (squares) and $Nd_2Fe_{12.2}Ga_{1.8}BD_{3.2}$ (circles).

Secondly, the enhancement of M_s upon D insertion is more pronounced at 300 K than at 4 K. This can be linked to the fact that at 300 K the temperature is closer to the T_C value. The increase of M_s at 300 K upon D insertion is twice that observed at 4 K (for $Nd_2Fe_{12.2}Ga_{1.8}BD_{3.2}$: +2 μ_B/f.u. at 4 K and +4.6 μ_B/f.u. at 300 K). This reflects the significant increase of T_C observed upon D insertion. As the D insertion induces an increase of T_C, the decrease of the magnetization due to the rise of temperature in the non-deuterated samples occurs before those of the deuterated samples. Even if the quantity of D inserted decreases upon Ga for Fe substitution, the enhancement of M_s upon D insertion is more pronounced in $Nd_2Fe_{12.2}Ga_{1.8}B$ than in $Nd_2Fe_{13}GaB$. Thus, we can conclude that the decrease of the M_s is not only induced by the replacement of a magnetic Fe atom by a non-magnetic one. As reported in Table 2, an increase of the mean magnetic moment per Fe atom has been determined by neutron diffraction. In the deuterated samples, the obtained value is equal to 2.8 μ_B. This moment is significantly higher than the mean magnetic moment previously observed in the pure alloys (2.5 μ_B [12]). This increase is important enough to compensate for the decrease of the magnetic moments carried by the Nd atoms occurring upon D insertion. The decrease of the Nd magnetic moments upon D insertion depends seriously on the Nd crystallographic site. A comparison of the Nd magnetic moments obtained in the alloys [12] and in the deuterated samples (Table 2) shows that the decrease of the Nd magnetic moments upon D insertion is more pronounced for the Nd ($4g$) atoms than for the Nd ($4f$) ones. This feature is evidenced whatever the Ga concentration is. For example in $Nd_2Fe_{13}GaB$, we have measured at 4 K a decrease upon D insertion of 1.1 μ_B and 0.3 μ_B for the Nd ($4g$) and Nd ($4f$) magnetic moments, respectively. The more notable influence of the D insertion on the magnetic moment carried by the Nd ($4g$) atoms can be linked to the measured inter-atomic distance. As shown in Table 3, the shortest Nd–D inter-atomic distances are the D_3–Nd ($4g$) and D_2–Nd ($4g$) ones. One can expect that the insertion of D atoms should influence more significantly the magnetic behavior of the Nd ($4g$) atoms than Nd ($4f$) ones.

The modifications of the magnetic moments carried by Nd atoms upon D insertion should also reflect a modification of the crystal electric field acting on the Nd sites. Other magnetic properties such as the temperature of spin reorientation [24] and the anisotropy parameters [6] are also known to be influenced by D insertion. Further investigations are in progress to probe these magnetic features.

4. Conclusion

The modification of the deuterium content uptake upon Ga for Fe substitution is analyzed in the light of two opposite effects of gallium.

- The increase of the unit cell volume induced by the Ga atom favors larger interstitial sites and consequently is favorable for the insertion of a larger amount of deuterium.
- The repulsive bonding effect D–Ga that may exclude the filling of interstitial sites by D atoms when the interstitial site environment is rich in Ga atoms.

Due to the preferential substitution scheme of Ga, the filling of the D interstitial sites exhibits a different behavior depending upon the crystallographic nature of the site involved.

The effects of the D absorption on the magnetic properties of the $Nd_2Fe_{14-x}Ga_xB$ are discussed as a function of the quantity of Ga atoms substituted. A link between the evolution of the shortest Fe–Fe inter-atomic distances upon D insertion and the increase of the Curie temperature is evidenced. Thus, the magnitude of the Curie temperature depends on both the quantity of deuterium inserted and the number of gallium atoms substituted. The atomic magnetic moments measured by neutron diffraction clearly exhibit an increase of the mean iron magnetic moment upon D insertion. The D insertion also induces a decrease of the magnetic moments carried by the Nd atoms. This effect is strongest for the Nd (4*g*) sites than for the Nd (4*f*) ones. Finally, the overall saturation magnetization increases upon D insertion in the $Nd_2Fe_{14-x}Ga_xB$ compounds.

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