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Abstract
The structural and magnetic properties of the $Gd_2Fe_{17}D_x$ compounds ($x = 0$, 3, and 5) have been investigated by means of x-ray powder diffraction, high energy inelastic neutron scattering and magnetic measurements. The $Gd_2Fe_{17}D_x$ compounds crystallize in the $R-3m$ space group with the Th_2Zn_{17}-like structure. The increase of the lattice parameters with D content reveals a two-step filling of the interstitial sites with deuterium first filling the octahedral 9e sites for $x = 3$ and then partially filling the tetrahedral 18g sites for $x = 5$. The evolution of the J_{ex} exchange coupling versus the deuterium (D) content is discussed. Although it is well known that the permanent magnet properties of D-doped samples are considerably better than those of the pure compound Gd_2Fe_{17} there is a reduction in the Gd–Fe exchange field. Finally, the influence of deuterium insertion on the exchange interaction between the Gd and Fe sublattice is compared to that of nitrogen (N) or carbon (C). The C and N atoms are found to be more efficient in reducing the intersublattice coupling.

(Some figures in this article are in colour only in the electronic version; see www.iop.org)

1. Introduction

The study of the physical properties of the rare-earth (R)–transition metal (T) intermetallic compounds is a major field of research in solid state physics. Some of these compounds have industrial uses, such as $SmCo_5$ or the $Nd_2Fe_{14}B$ phases which are produced for permanent magnet purposes.

    The knowledge of the inter-sublattice exchange interaction is of major interest in order to have access to a better understanding of the fundamental properties governing the R–T

intermetallic compounds. The inter-sublattice coupling strength is not easily predictable from other physical quantities. The reason for this is the complicated mechanism by means of which the exchange interaction between both sublattices is realized. The interaction between the R 4f electronic shell and the T 3d electrons is mediated by the 5d valence electrons of the R atoms. Thus, intra-atomic 4f–5d interactions and the inter-atomic 5d–3d hybridization play an important role as shown by band structure calculations [1, 2]. The R–T interaction has been shown to decrease significantly upon C or N insertion in the R_2Fe_{17} crystal structure [3]. Until now, nothing have been known about the effect of hydrogen insertion in this structure.

The inter-sublattice exchange interaction can in principle be deduced from the Curie temperatures of R–T compounds. This approach has been widely used for many R–T phases but this is an indirect method which only leads to an estimation of the inter-sublattice interaction. Furthermore, in the case of the hydrogen containing samples, this method is not applicable because the Curie temperatures cannot be accurately determined. In fact, the ordering temperatures are significantly underestimated since hydrogen starts to be released at temperatures lower than the Curie temperature. Another method to evaluate the R–T exchange interaction is the so called HFFP method (high field free powder), that is based on the application of a high magnetic field. This method is rather efficient but is only applicable if the magnetizations of the two sublattices are similar: magnitude of M_R close to M_T. Unfortunately, this is not the case of the R_2Fe_{17} or $RFe_{11}Ti$ phases for which the Fe sublattice magnetization is much larger than that originating from the R atoms.

In principle, deduction of R–T exchange interactions from Curie temperature measurements is possible as discussed elsewhere [4, 5]. But, in the case of the hydrogen or deuterium containing compounds, the desorption of the interstitial element may start to occur before reaching the Curie temperature [6, 7]. Consequently for the rare-earth–transition metal hydrides or deuterides, the measured Curie temperature has to be considered as an underestimation rather than an absolute measurement and the R–T exchange interaction deduced from the Curie temperature has to be considered as a rough estimation. Inelastic neutron scattering experiments on Gd compounds have the advantage that the energy transfers of the dispersionless spin wave mode (flat mode) are a direct measure of the exchange fields B_{ex} experienced by the Gd spins in the various types of Gd intermetallic [8–10].

As can be seen in figure 1, the insertion of D, C or N induces a spectacular modification of the Curie temperature in R_2Fe_{17} [11–14]. Many other magnetic properties are also dramatically modified by the presence of these interstitial elements:

- the saturation magnetization may be significantly increased

- the crystal electric field gradient experienced at the rare-earth site is also modified.

The influence of D on the physical properties of these hard magnetic materials has been analysed taking into account the location of the hydrogen within the crystal structure. The effect of hydrogen on the magneto-crystalline anisotropy of the R_2Fe_{17} [15] phases is opposite to that of carbon or nitrogen: hydrogen insertion induces a significant decrease of the rare-earth contribution to the anisotropy whereas C or N insertion induces a dramatic increase yielding the two new high performance permanent magnet materials $Sm_2Fe_{17}N_3$ and $Sm_2Fe_{17}C_3$ [11, 12, 15].

Here we focus on the investigation of the Gd–Fe exchange coupling by means of inelastic neutron scattering (INS) in $Gd_2Fe_{17}D_x$ ($x = 0, 3$ and 5) [16–19].
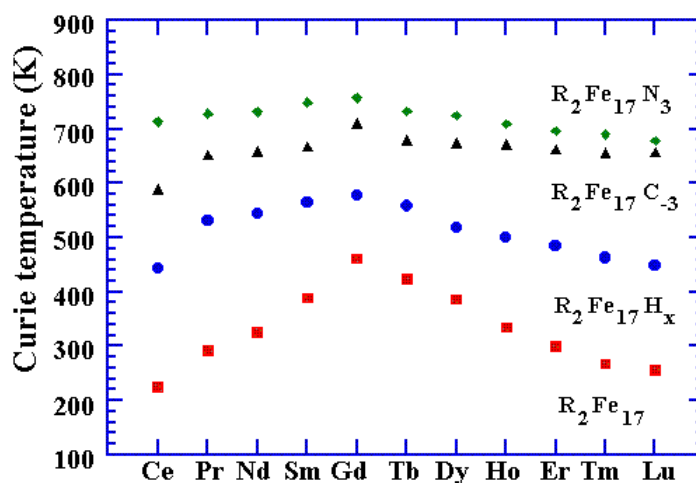
Figure 1. Curie temperatures of the R_2Fe_{17}, $R_2Fe_{17}H_x$, $R_2Fe_{17}C_{3-d}$ and $R_2Fe_{17}N_3$ compounds. The values for the $R_2Fe_{17}H_x$ phases are not reliable and have to be considered as an estimation (see text).

2. Experimental details

2.1. Sample preparation

The polycrystalline Gd_2Fe_{17} sample was prepared [13] by the induction melting technique in a cold copper crucible under an argon atmosphere, using elements of purity better than 99.95% for gadolinium and 99.99% for iron. In order to optimize the sample homogeneity small segments of the resulting ingot were wrapped in tantalum foil, sealed in an evacuated silica tube, and annealed at 1223 K for two weeks and then water quenched.

The insertion of deuterium in Gd_2Fe_{17} to form $Gd_2Fe_{17}D_5$ was performed at 423 K in a stainless autoclave under a hydrogen pressure of approximately 5 MPa. The deuterium content was controlled by measuring the change in deuterium vapour pressure in the autoclave and was determined by gravimetric analysis. The accuracy of the deuterium content is estimated to be about ±0.1 deuterium atoms per formula unit, an accuracy which has been confirmed [13, 20, 21] in related R_2Fe_{17} compounds by neutron diffraction studies. The preparation of $Gd_2Fe_{17}D_3$ was carried out by heating the appropriate mixture of Gd_2Fe_{17} and $Gd_2Fe_{17}D_5$ in a sealed tube. In order to both promote hydrogen diffusion and optimize the sample homogeneity, the sample was heated three times from room temperature to 570 K over a period of two to three hours. The resulting homogeneity of the sample was checked by conventional x-ray powder diffraction with iron $K\alpha$ radiation and, in all cases, less than approximately 5 vol.% α-Fe was found in each of the samples. High accuracy lattice parameters were determined with a Guinier-type focusing camera equipped with a monochromatic x-ray beam containing only iron $K\alpha_1$ radiation. (Silicon was added to the powder sample and used as an internal standard.) The diffraction patterns were recorded on x-ray film that was subsequently scanned with 20 μm steps in order to extract the relative diffraction intensities. The indexing of the Bragg peaks was performed on a hexagonal unit cell which is compatible with the rhombohedral $R-3m$ space group. The lattice parameters were then obtained by a least squares refinement using all the 25 observed Bragg reflections. This refinement leads to an accuracy of about ±0.002 Å for both lattice parameters a and c.

The magnetic ordering temperatures were determined with a Faraday torque balance with a sample heating and cooling rate of 5 K per minute. A sample of approximately 60 to 100 mg was sealed under vacuum in a small silica tube in order to prevent oxidation and/or decomposition of the sample during heating.

2.2. Inelastic neutron scattering

The experiment was performed on the high-energy transfer spectrometer (HET) at the UK spallation neutron source ISIS of the Rutherford Appleton laboratory. HET is a direct geometry chopper spectrometer [22] equipped with four ^{3}He detector banks, one lying at 4 m from the sample and covering a full scattering angle range $\phi = 3°–7°$, another is located at 2.5 m from the sample and spanning an angular range of between 10° to 30° and the other two providing data at large angles, $\phi = 115°$ and $\phi = 135°$. Incident energies from 30 to 2000 meV may be selected at the sample position by phasing a Fermi chopper to the 50 Hz source proton pulse. The neutron flux and resolution of the spectrometer can be varied by choosing different slit packages and rotation frequencies (in multiples of 50 Hz) for the chopper. This gives a wide choice of experimental configurations with high energy resolution and small scattering vector Q. The scattering function $S(Q, \omega)$ is obtained by sorting the signals from the detectors according to the scattering angle and the neutron time of flight. In the present experiment, the frequency of the Fermi chopper was set to its maximum value of 600 Hz for Gd_2Fe_{17} and $Gd_2Fe_{17}D_5$. This has led to a full width at half maximum (FWHM) of about 8 meV. A different experimental configuration was used for $Gd_2Fe_{17}D_3$ with a different set of slits and a chopper speed of 500 Hz. This reduced the FWHM to about 6 meV at the expense of a significant reduction in the neutron flux. Correction of the efficiency of the detectors was done using the scattering of a neutron white beam with a vanadium sample as standard.

The $Gd_2Fe_{17}D_x$ samples consisted of approximately 15 g of polycrystalline powder mounted in an aluminium can onto the cold plate of a closed-cycle refrigerator. Measurements were performed at 15 K with an incident energy of 250 meV. The specimen was prepared using Gd with natural isotopic composition, even though the presence of the strong ^{155}Gd and ^{157}Gd neutron absorption cross sections is not favourable. However, with the chosen incident energy, both incident and scattered neutrons have an absorption cross section sufficiently small to make the observation of magnetic excitations up to 50 meV possible. One has to keep in mind that in Gd_2Fe_{17}, iron represents 90% of the atoms contributing to a lower absorption cross section. Finally, deuterium isotope was used instead of hydrogen atoms in order to lower the incoherent scattering cross section.

Table 1. Position of the peaks observed by inelastic neutron scattering experiments on $Gd_2Fe_{17}D_x$ samples compared with $Gd_2Fe_{17}N_{2.7}$ and $Gd_2Fe_{17}C_x$ compounds. The corresponding exchange field B_{ex} at the Gd site and Gd–Fe exchange coupling constants are also reported. S_{Fe} and J_{ex} represent respectively the value of the spins and the exchange coupling constant between the Gd and Fe sublattice.
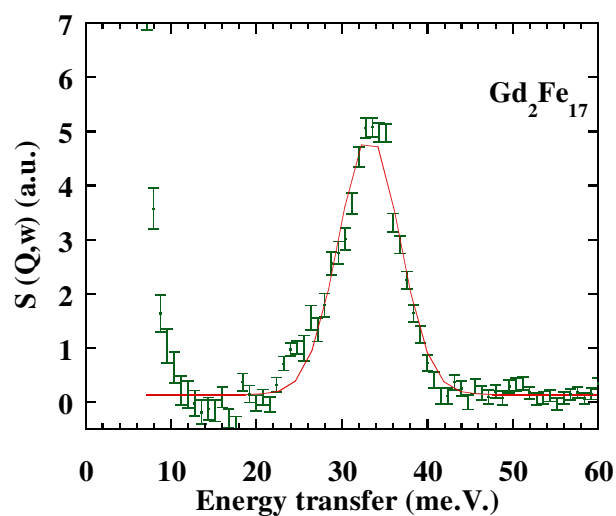
	Gd_2Fe_{17}		$Gd_2Fe_{17}D_3$	$Gd_2Fe_{17}D_5$	$Gd_2Fe_{17}N_{2.7}$[a]	$Gd_2Fe_{17}C_1$[a]	$Gd_2Fe_{17}C_2$[a]
Energy (meV)[b]	33.1 ± 0.1	33.0[a]	31.1 ± 0.1	28.7 ± 0.1	23.0[a]	30.2[a]	24.5[a]
S_{Fe}	1.05[a]		0.97	1.08	1.15[a]	—	—
$|J_{ex}|$ (meV)	0.83[a]		0.84	0.70	0.53[a]	—	—
B_{ex} (T)	285		268	247	199[a]	260[a]	211[a]

[a] Data from [1] and [9].
[b] The relative error on the determined energy is estimated to be 0.1 meV and the absolute error ranges typically from 0.5 to 1 meV.
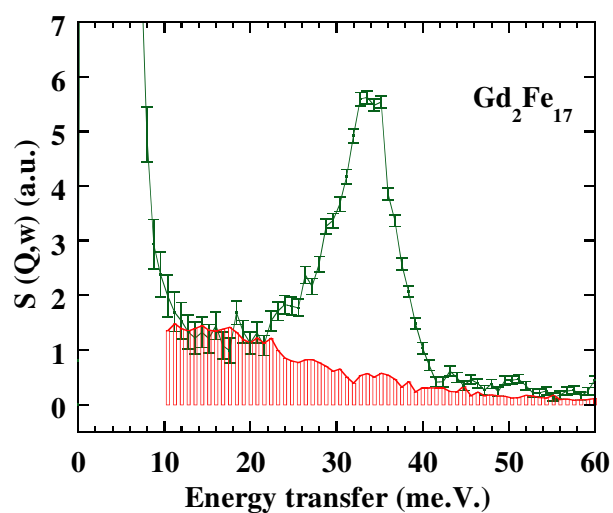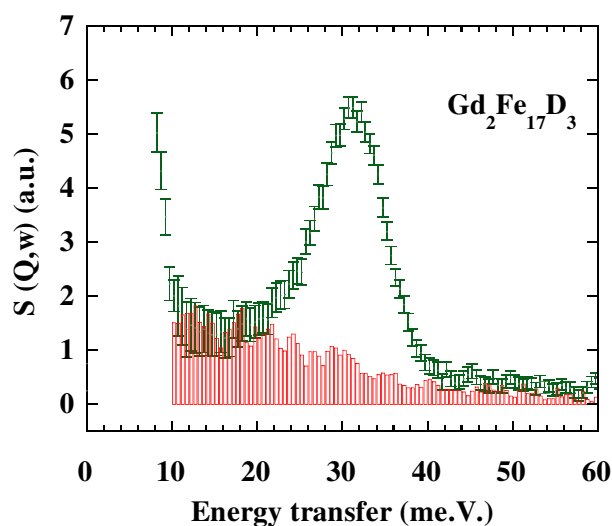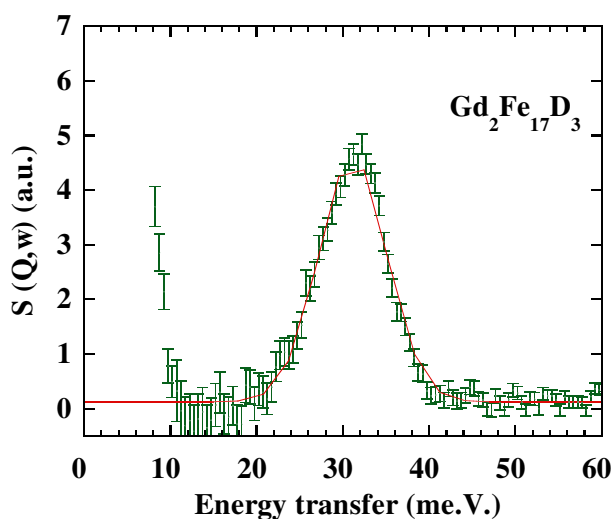
(a)

(b)

Figure 2. Inelastic neutron spectrum of Gd_2Fe_{17} at $T = 15$ K: (a) as measured; (b) after background subtraction. The shaded area in (a) indicates the non-magnetic inelastic intensity as deduced from the spectrum at high Q values. The incident neutron energy was 250 meV.

3. Results and discussion

In the INS spectra of the Gd_2Fe_{17}, $Gd_2Fe_{17}D_3$ and $Gd_2Fe_{17}D_5$ compounds (figures 2–4), a strong intensity maximum is seen at low momentum transfers representing the dispersionless spin wave mode. As can be seen in figures 2–4 as well as in table 1, our measurements have revealed that the Gd–Fe exchange interaction is reduced upon deuterium insertion. The solid line in the left part of figure 2 to 4 is a guide to the eyes. The shaded region shows the scattering determined from the high angle banks. This scattering is predominantly due to phonon processes as the magnetic scattering is small at such high momentum transfers.

Figure 3. Inelastic neutron spectrum of $Gd_2Fe_{17}D_3$ at $T = 15$ K: (a) as measured; (b) after background subtraction. The shaded area in (a) indicates the non-magnetic inelastic intensity as deduced from the spectrum at high Q values. The incident neutron energy was 250 meV.

The figures on the right display the magnetic signal after subtraction of the dispersive modes contributing to the background, with the line corresponding to a fit of the magnetic data. The estimation of all the dispersive modes has been deduced from the high Q values measured on the high angle banks and then subtracted from the signal, leading to figures 2(b), 3(b) and 4(b). It has been demonstrated in earlier work [8–10] that the main contribution to the non-dispersive mode observed in figures 2(b), 3(b) and 4(b) is the Gd–Fe exchange interaction.

One should note that an increase of the magnetization of the R_2Fe_{17} samples is observed upon saturating the interstitial sites with hydrogen or deuterium atoms. This magnetization
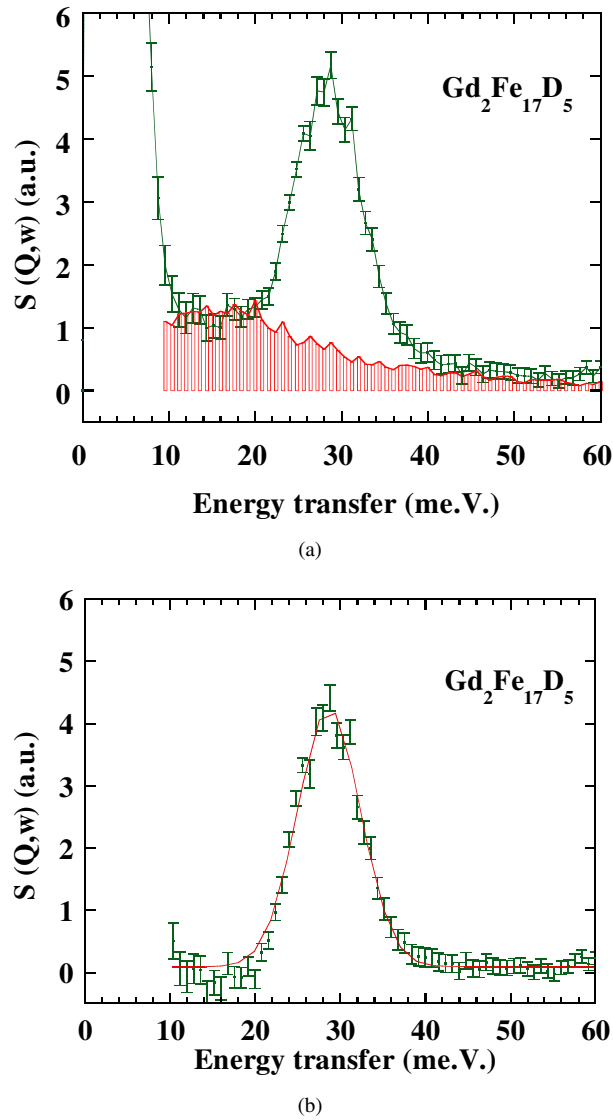
Figure 4. Inelastic neutron spectrum of $Gd_2Fe_{17}D_5$ at $T = 15$ K: (a) as measured; (b) after background subtraction. The shaded area in (a) indicates the non-magnetic inelastic intensity as deduced from the spectrum at high Q values. The incident neutron energy was 250 meV.

increase mainly happens on the Fe sublattice as was shown in [14, 23, 24]. In spite of this increase of the iron magnetic moment, INS measurements reveal that the exchange field at the Gd site decreases. The quantitative analysis of the INS data leads to a value of 33.1 meV for the energy of the flat mode in the Gd_2Fe_{17} sample. This value is in good agreement with that reported in [3] and [8]. For the samples containing deuterium atoms, the spectra indicate that the flat mode has been shifted to smaller energies. Thus, the R–T interaction is decreased by the doping. With nitrogen doping the energy decreases from 33 meV to 23 meV [3, 25], whereas we only see a shift from 33.1 meV to 28.7 meV in $Gd_2Fe_{17}D_5$. From that, we can conclude that the steeper the slope in figure 1 the larger the contribution of the

R–T exchange interaction to the value of the Curie temperature. Thus, considering the curves from bottom to top, the magnitude of the rare-earth–transition metal exchange interactions decreases.

The inelastic peak can be interpreted as being due to the excitation of the dispersionless spin wave mode that corresponds to out-of-phase precession of the Gd spins in the exchange field of neighbouring spins. Consequently, from the energy Δ of the inelastic neutron scattering signal, one can derive the corresponding exchange field B_{ex} at the Gd site or the exchange coupling constant J_{ex} between the Gd and Fe sublattices.

For the dispersionless mode, the relation between these quantities is

$$\Delta = \mu_B g_R B_{ex} = 2\,\mu_B B_{ex} = 2z J_{ex} S_{Fe} \tag{1}$$

with z being the number of Fe neighbours to the Gd ion ($z = 19$ for Gd_2Fe_{17}) and S_{Fe} representing the value of the Fe spin. A value of 2 was used for the Landé factor (g_R) of Gd. The J_{ex} and B_{ex} values obtained for the $Gd_2Fe_{17}D_x$ compounds are given in table 1. The formalism used here is detailed in [8] and [26].

The reduction of the Gd–Fe exchange interaction coupling upon D insertion is even more significant if we compare $Gd_2Fe_{17}D_3$ to $Gd_2Fe_{17}N_3$. Both samples have the same amount of interstitial elements and furthermore, for this concentration, D and N are both located on the same octahedral interstitial site [13, 20, 27]. Whereas $\Delta = 23$ meV in $Gd_2Fe_{17}N_3$, the corresponding value in $Gd_2Fe_{17}D_3$ is 31.1 meV. No value has been reported for the saturated $Gd_2Fe_{17}C_3$ sample, but the investigation of the $Gd_2Fe_{17}C_x$ ($x < 3$) compositions has demonstrated a considerable reduction of the exchange coupling upon C insertion into the Gd_2Fe_{17} crystal structure. Values of only 30.2 meV and 24.4 meV have been reported for $Gd_2Fe_{17}C$ and $Gd_2Fe_{17}C_2$ respectively [3]. This shows that C or N containing Gd_2Fe_{17} compounds exhibit similar reduction of the Gd–Fe exchange interaction whereas D insertion is less efficient.

The reduction of the Gd–Fe exchange interactions may be interpreted as being due to the increased cell volume reducing the hybridization/exchange interaction between the Fe 3d and Gd 5d electrons indirectly coupling the Fe 3d to the Gd 4f electrons. The same behaviour has already been observed upon nitrogenation. The values of the exchange field for the $Gd_2Fe_{17}C_x$ and $Gd_2Fe_{17}N_{2.7}$ compounds found in the literature are also reported in table 1 for comparison with the $Gd_2Fe_{17}D_x$ phases. It is remarkable that deuterium (hydrogen) is less efficient in reducing the R–Fe interactions than nitrogen insertion. A value of 199 T has been reported for the exchange field in $Gd_2Fe_{17}N_{2.7}$. A similar magnitude is also observed for the $Gd_2Fe_{17}C_x$ compounds whereas for $Gd_2Fe_{17}D_5$, the exchange field is still about 247 T. One has to remember that C or N insertion is inducing about the same volume increase of about 6% in the R_2Fe_{17} lattice, whereas D insertion leads to a much smaller cell increase of about 3%. This moderate cell increase may be the reason for the smaller effect of D insertion on the exchange field B_{ex}.

Table 2. Lattice parameters, Curie temperature and saturation magnetization of the $Gd_2Fe_{17}D_x$ compounds.

	a (Å)	c (Å)	V (Å³)	$\Delta V/V$ (%)	T_c (K)	M_s (μ_B fu⁻¹) (5 K)
Gd_2Fe_{17}	8.5386 (7)	12.4297 (10)	784.8	—	476	21.5
$Gd_2Fe_{17}D_3$	8.604 (1)	12.402 (2)	795.1	1.3	557	19.1
$Gd_2Fe_{17}D_5$	8.664 (2)	12.508 (2)	813.1	3.6	586	22.2

The increase of the unit cell that occurs upon D insertion in the Gd_2Fe_{17} lattice is highly anisotropic up to $x = 3$ favouring an expansion of the a and b lattice parameters rather

than along the c axis. For a hydrogen content higher than $x = 3$, the increase of the unit cell is observed both in the basal (a, b) plane and along the c axis. The lattice parameters determined for the $Gd_2Fe_{17}D_x$ phases are summarized in table 2. The evolution of the unit cell volume versus the D content is characteristic of a two step filling of the interstitial sites with deuterium first filling the octahedral 9e site for $x < 3$ and then, partially filling the tetrahedral 18g sites up to $x = 5$. This interpretation has been confirmed by *in situ* neutron diffraction study on the isostructural $Nd_2Fe_{17}D_x$ phases as discussed in [7]. It has been shown by Mössbauer spectroscopy that the weighted average hyperfine field at the Fe nucleus depends significantly upon the D concentration in the R_2Fe_{17} phases [28]. From Gd_2Fe_{17} to $Gd_2Fe_{17}D_3$ the observed reduction of the hyperfine field bears witness to a decrease of the mean Fe magnetic moment [29]. Then, for higher D content, $Gd_2Fe_{17}D_5$, the D atoms start to fill the tetrahedral interstitial sites, and the Fe hyperfine field increases [29]. It is noticeable that these results obtained by a microscopic technique (Mössbauer) [29] are in agreement with those obtained from macroscopic magnetization measurements reported in table 2. Unlike the Curie temperature which increases upon deuterium insertion (see table 2), the saturation magnetization of the $Gd_2Fe_{17}D_x$ phases is found to slightly decrease from 21.5 μ_B per formula unit for $x = 0$ to 19.1 μ_B per formula unit for $x = 3$ and then to increase up to 22.2 μ_B per formula unit for $x = 5$. It has been proved that the filling of the two interstitial sites by hydrogen (or deuterium) has different effects on the crystal structure [6, 7] and also on the magnetic properties such as the crystal electric field experienced at the rare-earth site [30], the saturation magnetization [14, 30] or the hyperfine field experienced at the iron nucleus [28, 29]. It is interesting to compare how the progressive filling of the octahedral and then of the tetrahedral sites modifies the Gd–Fe exchange interactions in order to determine if the two interstitial sites have the same effect on this exchange interaction or not. According to our INS experiment the exchange field decreases continuously with deuterium versus the deuterium content. Unlike other magnetic properties such as the Fe hyperfine field [28, 29], crystal electric field at the rare-earth nucleus [30] or the saturation magnetization [14], the variation of the exchange field at the Gd site does not depend on the interstitial site occupied by the deuterium atoms. If one looks at the J_{ex} Gd–Fe exchange coupling constant, the tendency is more complex. Since the insertion of three deuterium atoms induces a reduction of the iron magnetization, the J_{ex} exchange coupling is found to be the same for Gd_2Fe_{17} and $Gd_2Fe_{17}D_3$ (0.83 meV). For higher D concentration the saturation magnetization increases and the J_{ex} parameter decreases to 0.70 meV. As can be seen from table 1, this decrease is significant but remains smaller than that induced by N insertion. The rather weak sensitivity of the J_{ex} value to the occupancy of the octahedral interstitial site by deuterium (or hydrogen) is remarkable in comparison to what happens when C or N fill these sites. This may be due to the fact that unlike C or N, deuterium atoms do not strongly bond to the iron atoms surrounding the Gd site. The strong bond of C or N with the neighbouring Fe atoms has been shown to reduce significantly the magnetic moment of the nearest Fe atoms [31, 32]. The origin of this decrease of the Fe magnetic moment upon hybridization with the interstitial C or N elements has been discussed in detail elsewhere [33]. In the case of D or H, the insertion is mainly driven by the attraction by the rare-earth element because of the large difference in the electronegativity between the rare earth and D (or H).

It is to be noticed that unlike the $Gd_2Fe_{17}C_x$ and $Gd_2Fe_{17}N_{2.7}$ compounds which exhibit [3] several distinct excitations characteristic of different C or N concentrations, the $Gd_2Fe_{17}D_x$ compounds have been found to exhibit only one magnetic excitation. The width of this unique magnetic excitation corresponds to the experimental resolution, indicating that a unique exchange field is experienced at all Gd sites. This can be regarded as a further proof of the homogeneity of the deuterium containing samples $Gd_2Fe_{17}D_3$ and $Gd_2Fe_{17}D_5$.

4. Conclusions

For the first time to our knowledge, the magnetic inter-sublattice exchange coupling of rare-earth–transition metal hydride (or deuteride) has been directly probed by inelastic neutron scattering. As already observed for other interstitial elements such as C or N, D insertion reduces the exchange field B_{ex} at the Gd site. B_{ex} is found to decrease from 285 T for Gd_2Fe_{17} to 247 T for $Gd_2Fe_{17}D_5$. This reduction is much weaker than that for C or N insertion in the Gd_2Fe_{17} crystal structure. This has been related to the much smaller increase of the unit cell volume by D insertion in comparison to that of C or N.

In spite of a significantly larger overall iron magnetic moment in $Gd_2Fe_{17}D_5$ compared to Gd_2Fe_{17}, an important decrease of the exchange interactions experienced at the Gd site is observed. The determination of the J_{ex} exchange coupling constant has revealed that the insertion of D atoms in the octahedral interstitial sites has almost no influence on J_{ex} whereas when the tetrahedral interstitial sites are filled the J_{ex} value drops significantly.

Acknowledgments

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