NMR study of GdFe$_2$H$_x$ hydrides

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Abstract

NMR study of GdFe$_2$H$_x$ ($x = 0$, 1.05, 1.7, 2.45, 2.85) hydrides are reported. The values of x chosen at characteristic points of the phase diagram correspond to single phase compounds. Spin echo spectra at zero field and relaxation times T_2 have been measured on powder samples at 4.2 K. The resonances of ^{155}Gd, ^{157}Gd and ^{1}H have been identified and the values of the hyperfine fields are obtained. The results are analysed in terms of hydrogen occupation of A2B2 sites and a comparison of hydrogen hyperfine field with dipolar fields at H sites evaluated from lattice sums is made.

Rare earth-iron intermetallics have recently attracted renewed interest of researchers owing to their capability of hydrogen uptake. One of the problems related to the presence of hydrogen in their structure concerns modification of their structural, electronic and magnetic properties. The compound GdFe$_2$ crystallizes in C15 structure with space group *Fd-3m*. It preserves this structure with hydriding up to $x = 3.5$ [1]. The values of x have been chosen at characteristic points of the phase diagram which correspond to single phase compounds [2]. Recent neutron diffraction study has shown that hydrogen in the REFe$_2$ compounds occupies mostly the A2B2 (RE2Fe2) tetrahedral sites [3]. In order to study the influence of hydrogen uptake on the electronic and magnetic properties at the level of sites of individual elements in the structure an NMR study has been undertaken.

Spin-echo spectra and relaxation times T_2 were measured at 4.2 K with an automated, frequency swept spin-echo spectrometer [4]. Polycrystalline powder samples of GdFe$_2$H$_x$ with $x = 0$, 1.05, 1.7, 2.45, 2.85, the same as in [2] were used. Relaxation time T_2 was measured at the maxima of the spectra. The spectra obtained are presented in Fig. 1.

The spectra for $x = 0$ and 1.05 exhibit two narrow resonances at the frequencies of 57.09 and 74.82 MHz for GdFe$_2$ and 56.95 and 74.56 MHz for the sample with $x = 1.05$. As the ratio of the two resonant frequencies in each spectrum corresponds to the magnetogyric ratio of the two gadolinium isotopes, ^{155}Gd and ^{157}Gd, the lines were attributed to these isotopes. Although both isotopes have spin 3/2, no quadrupolar splitting was observed on these lines, which is due to a cubic symmetry of the gadolinium site in the structure. For the compound with $x = 1.05$ the two lines observed are attributed to Gd sites with no hydrogen as a nearest neighbour. A small population of such sites is reflected in the absolute intensity of the spectrum for the compound with $x = 1.05$, which is an order of magnitude smaller than that of the unhydrided compound.

Relaxation time T_2 slightly differs between the two isotopes and for the ^{155}Gd resonance line at 57 MHz T_2 is of 1 ms, whereas for the ^{157}Gd resonance line at 75 MHz T_2 is 10% lower.

The Gd hyperfine field values were obtained from the resonant frequencies, ν, by using the formula $B_{hf} = \nu\gamma_n$, where γ_n is the nuclear magnetogyric ratio for a Gd isotope. B_{hf} amounts to 43.66 T for $x = 0$ and 43.54 T for $x = 1.05$. A slightly smaller hyperfine field in the hydrided compound is

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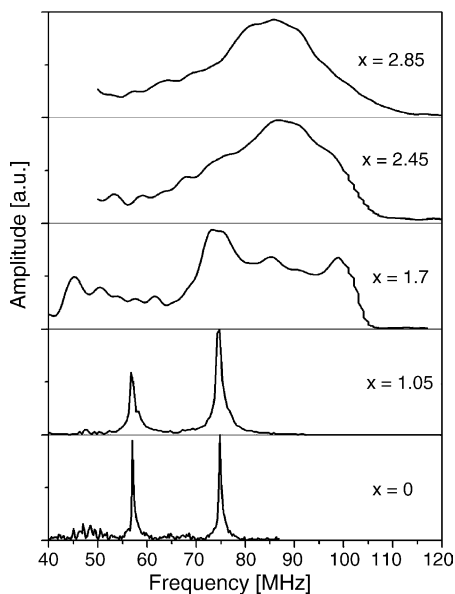*E-mail address:* vpro8220@mbox.troja.mff.cuni.cz (V. Procházka).

Fig. 1. NMR spin echo spectra of $GdFe_2H_x$ ($x = 0, 1.05, 1.7, 2.45, 2.85$) at zero external field and 4.2 K. The maximum signal in each spectrum is set to unity.

Table 1
Absolute values of the dipolar field, H and its components H_x, H_y and H_z

$H(T)$	N	$H_x(T)$	$H_y(T)$	$H_z(T)$
1.05	8.00	−0.25	−0.71	0.73
1.05	8.00	−0.71	−0.25	0.73
1.05	8.00	−0.25	−0.71	−0.73
1.05	8.00	−0.71	−0.25	−0.73
1.95	8.00	1.13	1.13	−1.11
1.95	8.00	1.13	1.13	1.11
2.03	16.0	−1.44	−1.44	0.00
2.07	8.00	0.40	0.86	1.84
2.07	8.00	0.86	0.40	1.84
2.07	8.00	0.40	0.86	−1.84
2.07	8.00	0.86	0.40	−1.84

N denotes the number of A2B2 sites in the unit cell exhibiting the same value and direction of the field.

for Fe moments were taken and their antiparallel alignment was assumed.

The NMR signal at zero field corresponds predominantly to domain wall edges, where the directions of magnetic moments are close to those in magnetic domains [5]. Therefore we can relate the number of the resonance lines in the hydrogen spectrum with the number of magnetically inequivalent hydrogen sites for a particular easy magnetisation direction. The presence of four lines in the spectrum for $x = 1.75$ indicates that the easy magnetisation direction in this compound is (1 1 0). A dominant single line in the spectra for $x > 1.75$ indicates that the easy magnetisation direction is possibly changed with increasing hydrogen content to (1 0 0). The values of dipolar fields presented in Table 1 corresponds to such directions of magnetic moments.

It is worth noting, that dipolar field values are systematically lower than the hyperfine fields obtained from the experiment. This indicates presence of a Fermi-contact-like contribution from s-electron density at the hydrogen site amounting to −0.13 T.

due to an increase of interatomic distances related to lattice expansion caused by hydrogen uptake. The hyperfine field at Gd nuclei with hydrogen atoms in the nearest neighbourhood according to Mössbauer measurement is lower than in the unhydrided compound [1]. An NMR study of isostructural YFe_2 hydrides shows a dramatic influence of hydrogen neighbours on the yttrium hyperfine field [5]. Five hydrogen neighbours decrease hyperfine field by as much as 87%. As hydrogen neighbours produce also an electric field gradient at adjacent Gd sites, it causes an extreme broadening of Gd resonance and the sites with hydrogen neighbours are not observed in the NMR spectra. This explains why Gd resonances for $x > 1.05$ are not observed.

Broad spectra in the 40–110 MHz range are obtained for the compounds with $x > 1.05$. As they exhibit T_2 an order of magnitude smaller than that of Gd lines, and their intensity increases with increasing x, they are attributed to hydrogen resonance. The ^1H spectrum for the compound with $x = 1.7$ consists of several overlapping peaks which collapse into an unresolved broad line with further increasing x. The hyperfine field at hydrogen site determined from the central frequency for the compounds with $x = 2.85$ amounts to 2.1 T and for $x = 1.7$ it ranges from 1.8 to 3 T. The relaxation time T_2 was found to be an order of magnitude shorter than for Gd resonances and it amounts to 125 μs for $x = 1.7$ at 76 MHz, 100 μs at 88 MHz and 150 μs at 91 MHz. For the compounds with $x = 2.45$ and 2.85 it amounts to 72 μs at 90 MHz and 65 μs at 87.6 MHz, respectively.

It is commonly accepted that the hyperfine field at hydrogen is mostly of dipolar origin. In order to compare the experimental values to the theoretical ones, magnetic dipolar fields were calculated for A2B2 sites and various easy magnetization directions. The values of $7\mu_B$ for Gd and $1.5\mu_B$

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