

NMR STUDY OF $Gd_2Fe_{17}N_x$ INTERMETALLIC COMPOUNDS*

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ABSTRACT

The ^{57}Fe , ^{155}Gd and ^{157}Gd NMR of $Gd_2Fe_{17}N_x$ was measured in the ordered magnetic state at 4.2 K for $0 \leq x \leq 3$. The NMR signal intensities fall with increasing nitrogen content. The ^{57}Fe lines were found to move to higher frequencies with increasing x in agreement with Mössbauer experiments. The nitrogenation of the particles was found to be inhomogeneous.

Key-words: NMR; Nitride; Gd.

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The $\text{Gd}_2\text{Fe}_{17}$ intermetallic compound crystallizes with the $\text{Th}_2\text{Zn}_{17}$ structure (rhombohedral) [1]; the magnetization is perpendicular to the c axis [2], and the ordering temperature is almost 500 K. As it reacts with nitrogen, $\text{Gd}_2\text{Fe}_{17}\text{N}_{3-x}$ (or shortly, $\text{Gd}_2\text{Fe}_{17}\text{N}_3$) is formed, with the same crystal structure and a magnetic ordering temperature of 758 K [1]. Nitrogen atoms can occupy almost completely the 9e interstitial positions, located near the Gd atoms, in the c plane. With nitrogenation, a substantial drop in the magnetic hyperfine field and a large increase in the electric field gradient was observed at the Gd site by Mössbauer experiments [3]. Large changes in the hyperfine interactions at the R sites were also observed in Y_2Fe_{17} and $\text{Sm}_2\text{Fe}_{17}$, but in the opposite direction [4].

The compounds were prepared in an arc furnace, from high purity components (Fe 99.99% and Gd 99.9% purity, supplied by Johnson Matthey). The samples were heat treated at 1100°C for 10 days, crushed, milled in a planetary ball mill, and then heated in a nitrogen atmosphere (purity 99.999%) at 400°C.

The zero-field pulsed NMR measurements were performed at 4.2 K with two different automated spectrometers; one for measurements below 100 MHz, and the other [5] above 100 MHz.

The NMR spectra for $\text{Gd}_2\text{Fe}_{17}\text{N}_x$ are shown in figure 1. As x increased the intensity of NMR signals fell, because the nitrated regions are magnetically hard [6], and longer signal averaging was required to obtain the spectra. The lines near 46.7 MHz and 217.7 MHz are attributed to free Fe and Co which are known to segregate during the course of nitrogenation. The Co is present originally as an impurity in the Fe at very low concentration but the NMR signal is some 10^5 times stronger than from an equal mass of Fe.

The ^{57}Fe Mössbauer results (at 15 K) show hyperfine fields in the pure compound ($x = 0$) and in the saturated nitride ($x \approx 3$) that correspond to frequencies ranging from 40 to 54 MHz [7]. Starting from these results, the NMR spectra allow a more detailed analysis of the effects of nitrogenation, due to the higher resolution, and also because the Fe resonances show no quadrupole interaction.

There are 7 magnetically inequivalent Fe sites in $\text{Gd}_2\text{Fe}_{17}$ with the rhombohedral structure but only two ^{57}Fe lines are observed in the pure $\text{Gd}_2\text{Fe}_{17}$ sample, at frequencies of 47.68 MHz and 51.29 MHz which are thought to come from the 9d and 6c sites respectively. As nitrogen is added, these lines show a slight ($\approx 1\%$) increase in frequency as a function of N concentration. They seem to arise, in the samples with $x > 0$, from regions of practically pure (i.e. non-nitrated) compound.

With the process of nitrogenation, three new lines appear, reaching, for $x=3.0$, the frequencies 45.83 MHz, 50.49 MHz and 53.43 MHz. They correspond to the sites 18h, 9d and 6c, in the nitride, if we adopt the assignment made from the analysis of the Mössbauer spectra [7].

Two intense lines observed in $\text{Gd}_2\text{Fe}_{17}$ near 55 MHz and 60 MHz are due to ^{155}Gd and ^{157}Gd NMR (Fig. 1). The full Gd spectrum contains other lines, since for both isotopes $I=3/2$ and the electric quadrupole interaction is comparable to the magnetic interaction. The simulated spectra computed with the Mössbauer hyperfine parameters [8] gave fair agreement with the present NMR results.

Lines near 108 MHz and 130 MHz, also attributed to the Gd isotopes, are present throughout the series. For pure $\text{Gd}_2\text{Fe}_{17}$, the frequencies are: 107.7 MHz (^{155}Gd) and

129.4 MHz (^{157}Gd). New lines around 140 and 255 MHz increase in relative importance with increasing x . The fully nitrated compound $\text{Gd}_2\text{Fe}_{17}\text{N}_3$ presents a weak line at 254.8 MHz. This high frequency line appears in the region where the Gd lines are predicted for the nitrides, on the basis of the Mössbauer results [8]. Two weak lines near 250 MHz in the pure compound may be due to a small fraction of $\text{Gd}_2\text{Fe}_{17}$ in the hexagonal $\text{Th}_2\text{Ni}_{17}$ structure; the coexistence of the two structures for the Gd compound has been reported before [2].

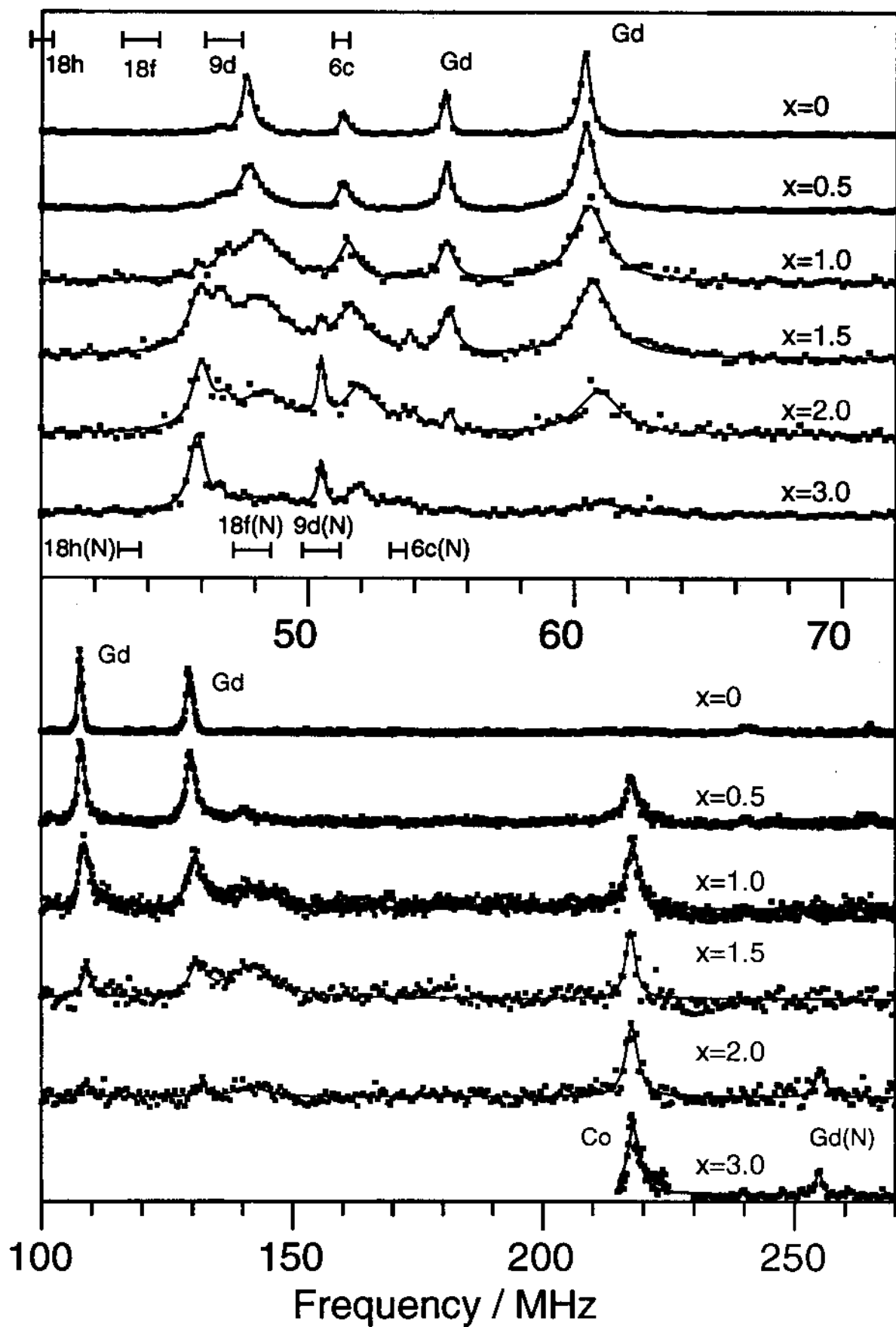
The NMR measurements with samples of nitrated intermetallic compounds of the series $\text{Gd}_2\text{Fe}_{17}\text{N}_x$ have shown that the signals fall with increasing concentration of N, a fact associated to lower domain wall mobility, which also leads to an increase in coercivity of the nitrated regions of the compounds. The Fe spectra corresponding to the pure compound and the nitride vary only slightly in frequency, as a function of concentration. The small shift of each line, as a function of x , may arise either from changes in the electronic structure, or from stress due to the inhomogeneity in lattice parameter introduced with nitrogenation [9]. The average ^{57}Fe hyperfine field increases as a function of nitrogen concentration, as observed in other compounds of the same series (e.g. [10]).

The observation of ^{57}Fe hyperfine fields corresponding to pure $\text{Gd}_2\text{Fe}_{17}$ intermetallic compounds for average nitrogen concentrations near the saturation value reinforces the picture of an inhomogeneous process of nitrogenation in these systems [11]. The H_{hf} of the 6c site of the unreacted material changes by about 1% in the whole concentration range. The 6c site line of the nitride appears at frequencies some 5% higher. Mössbauer studies on the $\text{R}_2\text{Fe}_{17}\text{N}_x$ nitrides do not have the resolution to observe this distinction between sites, for the same concentration.

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CAPTIONS

Fig. 1 NMR spectra of $\text{Gd}_2\text{Fe}_{17}\text{N}_x$ at 4.2 K. The continuous lines are computer fits to a sum of lorentzian lines. The horizontal lines show the Fe line positions predicted from the Mössbauer data.



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