

^{57}Fe NMR Study of Nitrided $\text{Ce}_2\text{Fe}_{17}$ *

by

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ABSTRACT

The ^{57}Fe NMR of $\text{Ce}_2\text{Fe}_{17}\text{N}_x$ ($x = 0 - 1.5$) was measured in the ordered magnetic state at 4.2 K. For $x = 0$, resonances coming from all Fe sites have been identified in the 30 - 45 MHz range. With nitrogenation, new lines appear in the range 37 - 54 MHz. Every nitrogenated sample shows three sets of lines, arising from regions where Ce atoms have 0, 2, and 3 nitrogen atoms as near neighbors.

Key-words: NMR, $\text{Ce}_2\text{Fe}_{17}\text{N}_x$.

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In this work we explore the high resolution of NMR to gain direct information on the nature of the nitrogenation process and its influence on the magnetic moments at the four inequivalent Fe sites in the $\text{Ce}_2\text{Fe}_{17}\text{N}_x$ system, studying the local consequences of nitrogenation. Few NMR studies on similar nitrogenated systems have been published; they were turned mainly to the R sites (Sm [1], Y [2] and Gd [3]).

This work concerns the initial stage of nitrogenation. The starting compounds and the nitrides were prepared and characterized as described elsewhere [4]. The nominal compositions were $x = 0.0, 0.5, 1.0$ and 1.5 . X-rays diffraction confirms that the original rhombohedral (RHO) structure is preserved and detects the presence of α -Fe precipitates after N uptake.

The NMR measurements were done at 4.2 K in zero external field, as in [3]. The dependence on the repetition rates and rf power of the relative signal intensities has been used for line identification.

The spectra of ^{57}Fe in all the studied samples cover the 25 - 60 MHz frequency range. ^{57}Fe resonances in $\text{Ce}_2\text{Fe}_{17}$ are in the 25 - 45 MHz range. Nitrogenation produces new lines in the range 37 - 54 MHz.

Fig. 1 shows for $\text{Ce}_2\text{Fe}_{17}$ two groups of ^{57}Fe NMR lines. We assign the strongest spectrum in the range 32 - 36 MHz, the large peak around 44 MHz (not shown, since it was obtained with different excitation conditions) and the small peak near 40 MHz to nuclei in the dominant RHO phase. The weak signals in the range 27 - 31 MHz may belong to a small amount of hexagonal phase (HEX); this phase will be not be discussed here.

Each of the lines in the 32-36 MHz range shows marginally resolved features on the low and high-frequency sides. These can be attributed to: a) nuclei within in-plane domain walls with Fe moments in the c-plane, or b) nuclei in magnetically different environments. Since ^{57}Fe has $I = 1/2$ there are no quadrupolar effects.

Mössbauer Spectroscopy (MS) probes essentially Fe nuclei in bulk of domains. We observe NMR of domain wall edge signals (as in $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ [1]), whose frequencies are essentially the same as those of the domains. As a consequence, the main RHO peaks we observe at ~ 33 and ~ 35 MHz have to be attributed to the 18h and 18f sites, respectively. The other two sites are in agreement with the B_{hf} values obtained by MS [5] (we have used the factor $\gamma/2\pi = 0.13757$ MHz/kG). The observed structures come from the related magnetically different sites.

The sequence in B_{hf} values: $6c > 9d_{1,2} > 18f_{1,2} > 18h_{1,2}$, according to the number of Fe and Ce nearest neighbors, is confirmed [5].

Neutron diffraction studies show that N atoms enter only into the 9e interstitial sites and it is known that there are no topological modifications of the rhombohedral structure with insertion of N, but a strong increase in T_c as a consequence of volume expansion.

Marked modifications in the hyperfine (hf) field distribution are observed when N is absorbed: 1) two new groups of lines appear in the ranges 37 - 46 MHz and 47 - 54 MHz; 2) lines already assigned to pure $\text{Ce}_2\text{Fe}_{17}$ are still present with decreasing intensity, even in the more N-concentrated samples; 3) lines with the highest B_{hf} values are also present, even for the less N-concentrated sample; 4) even for small x , a strong resonance (not present in the pure sample) around 46.6 MHz coming from α -Fe precipitates, is observed. The concentration of this phase increases rapidly as more N is absorbed.

To summarize, this ^{57}Fe NMR study in partially nitrogenated $\text{Ce}_2\text{Fe}_{17}\text{N}_x$ compound evidences, for every sample ($x = 0.5 - 1.5$), the coexistence of at least three very well defined regions: 1) region I, the non-nitrogenated zones with Fe sites as in the pure compound; 2) region II (37 - 46 MHz), has to be assigned to the zones in the compound where the 9e sites are partially filled with N atoms; 3) region III (47 - 54 MHz), with $B_{hf} = 39.3$ T for the 6c site, higher than other previously reported. Published values for samples with x near 3, where all 9e sites are practically full, are close to our result. We suggest that our samples have regions where the 'local' concentration x is close to the ideal value 3.

Two models for the nitrogenation mechanism of these compounds have been proposed (see e.g., [4], and references therein). The present observations show that the nitrogenation mechanism is consistent with a model which takes into account a) a step function concentration gradient for the diffusion process, and b) occupation of the 9e site not in accord with the binomial distribution.

For $x = 0$, the NMR signal from the 18f and 18h sites decreases smoothly as the rf is attenuated. For $x \geq 0.5$ the echo intensity passes through a broad maximum when the rf is strongly attenuated and after that it decreases rapidly. This result indicates that at these sites the magnetic anisotropy constant has been considerably reduced with the N insertion.

In partially nitrogenated samples, we can have Ce environments with 0, 1, 2 and 3 N as nn. In $\text{Ce}_2\text{Fe}_{17}$ and $\text{Ce}_2\text{Fe}_{17}\text{N}_{2.6}$ the macroscopic magnetization is known to be in the basal plane. For the 6c site, the principal axis of the EFG tensor is parallel to the c -axis and makes 90° with B_{hf} , with zero asymmetry parameter.

From these observations, we suggest that the "regions" we see through ^{57}Fe NMR are those where Ce atoms have 0, 2 and 3 N atoms as neighbors. Sites with 1 N nn are not observed because of strongly pinned domain walls, as indicated in [1]. No comparable observation was made in the other published NMR work with data on the ^{57}Fe sites in R_2Fe_{17} compounds [3].

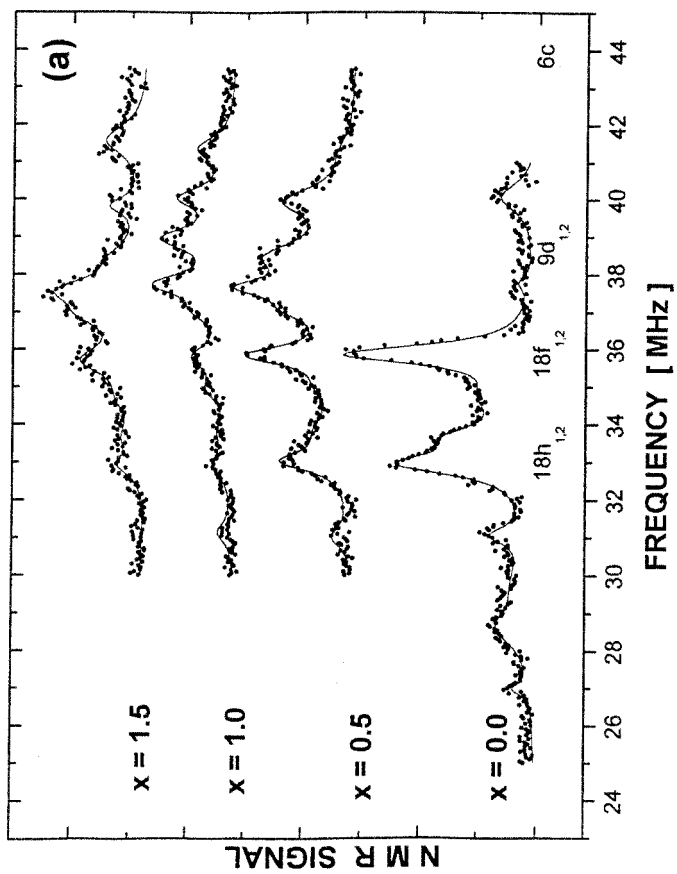
This conclusion seems to show the existence of regions in the sample where N is statistically distributed in the lattice sites. Our results, therefore, are in agreement with a description that contains elements of both models for nitrogenation [4]; this point, however, needs more detailed studies to be clarified.

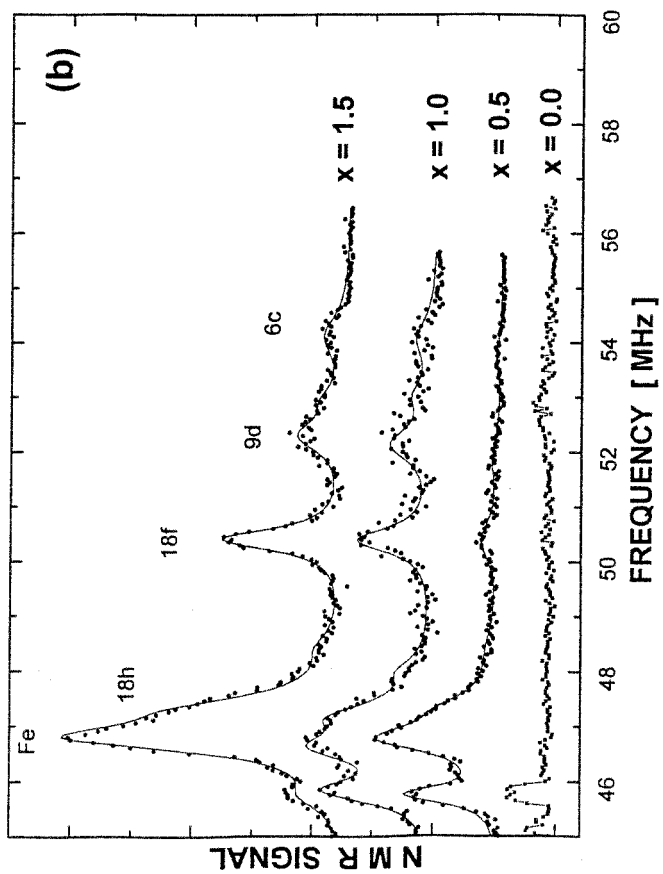
For the regions identified in $\text{Ce}_2\text{Fe}_{17}\text{N}_x$, the magnitude of the increase in B_{hf} depends on the Fe site; e.g., within region I (Ce with 0 N as nn) and region III (Ce with 3 N nn), as expected, 18f sites suffer the most important change ($\sim 11T$) since they are very near the N atoms, and 6c sites are less affected, ($\sim 7.3T$).

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Figure Captions

Fig. 1 ^{57}Fe NMR spectra of $\text{Ce}_2\text{Fe}_{17}\text{N}_x$ at 4.2 K, in the initial stages of nitrogenation, a) in the low-frequency region; b) in the high-frequency region.





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