# NMR Measurements in Milled RE-TM$_2$ Compounds (RE= Gd and TM= Co, Fe)*

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## ABSTRACT

Milled samples of the Laves phase intermetallic compounds GdFe$_2$ and GdCo$_2$ were measured by NMR at 4.2 K. The milling was made from the crystalline intermetallic compounds, inside a cylindrical tool made of hard steel, under argon atmosphere, for several different time intervals. The initial compounds were produced from high purity elements in an arc furnace, under inert atmosphere. Their X-ray diffraction patterns agreed with those of the literature. The milling of GdFe$_2$ and of GdCo$_2$ induces amorphization. Above 1 hour the milling of GdFe$_2$ leads to segregation of $\alpha$-Fe and formation of a Gd-Fe phase. These results are shown in the X-ray analysis. The spin-echo pulse NMR technique was utilized to study some structural and magnetic properties as a function of milling time. The measurements were made in a broad band pulse NMR spectrometer. The NMR spectra of the $^{155}$Gd and $^{157}$Gd isotopes in GdFe$_2$ show a broadening and displacement of the NMR lines, reflecting the introduction of defects, some kind of disorder and also the formation of a new Gd-rich phase after 1 hour. This result is in agreement with the X-ray spectra. In both systems, the spectra of the amorphous samples show broader lines, and the measured hyperfine fields do not change much with milling.

Key-words: NMR; Milling; Intermetallic compounds; RE-TM; GdFe$_2$; GdCo$_2$.

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## 1. Introduction

The high energy milling method to prepare amorphous, micro- and nano-crystalline materials has been increasingly applied in the recent years[1,2]. Milling may overcome some of the difficulties found in other methods to prepare materials in the metastable states, such as melt-spinning, condensed vapor and sputtering, because it may start from elements insoluble in the liquid state, or just out of a compound stoichiometry, to get bulk powder disordered materials. Solid state reaction induced by severe milling has proved to be a convenient method to prepare metastable powder samples starting from powders of pure chemical elements. In the present work, we have milled some Laves phase intermetallic compounds, with the aim of obtaining metastable disordered alloys that were analyzed in terms of their structural and hyperfine properties.

## 2. Experimental

The compounds $RT_2$ (R = Y, Gd and T = Fe, Co) were prepared by arc melting from the pure elements under argon atmosphere. The alloy buttons obtained were sealed in evacuated quartz tubes, then annealed during 90 hours at 850 $^{o}$C and quenched in cold water. To reduce the possibility of having undesirable phases in the initial samples, a thin layer was filed off from the surface of the buttons. Small pieces taken from the buttons were mixed together, and then powdered for X-Ray and NMR analysis. Samples for Mössbauer spectroscopy were also separated; the results were sent for publication elsewhere[1,3].

The milling procedure of each compound took the following steps: in a glove box filled with pure argon gas, about 9 grams of the compound were sealed in a hardened steel vial (hardness of HRc = 65 ± 1). The vial has cylindrical shape and internal dimensions of 4.0 cm height and 7.2 cm diameter. The milling tool used was a massive cylinder of the same material, covering 43% of the vial internal volume. To prevent air from entering the vial during the milling procedure, an o'ring-sealed and screwed top was used. Subsequently, the sealed vial was placed in a commercial vibrating frame machine, and during the milling the vial temperature was kept around 320 K. Samples were collected after various pre-established times and were labeled with the actual milling time. The maximum milling times were 50 hours for the Y compound[1], 100 hours for $GdCo_2$ and 276 hours for $GdFe_2$. To collect the samples, the vial was taken from the vibrating machine and opened inside a glove box filled with argon gas. While under the argon atmosphere, the collected powder was closed in a small container for XRD and NMR analysis. In order to avoid contamination and the possibility of a room temperature annealing of the phases present in the samples, the collected samples were kept at liquid nitrogen temperature when not in use.

The results of XRD and NMR for the YFe alloy were discussed elsewhere[1] and will be used here mostly for comparison.

X-ray spectra were obtained with a conventional diffractometer using a Co tube. Some sample compositions were also checked using scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDS).

The NMR measurements were performed using the zero-field spin echo technique, at 4.2 K. A home made automated spectrometer was used. The typical pulse sequence consisted of two 0.5 μs pulses; each NMR spectrum required from 1 to 20 hours of measurement. The NMR measurements detected resonances from $^{59}$Co, $^{57}$Fe, $^{155}$Gd and $^{157}$Gd nuclei.

## 3. Results and Discussion

X-ray diffraction patterns clearly show that a strong segregation has occurred after few hours of milling in the cases of $GdFe_2$, $GdCo_2$ and $YCo_2$; for $YFe_2$ no segregation has appeared and only an amorphous phase was detected with 50 hours of milling[1]. In the samples where segregation has occurred this effect is noticeable within the first hours of milling: one hour in the case of $GdFe_2$ and about 5 hours in the samples with Co. For longer milling times a continuous broadening of the X-ray diffraction peaks indicated a reduction of the grain sizes; in addition, $^{57}$Fe Mössbauer results[3] in $GdFe_2$ have shown the formation of a disordered phase between Gd and Fe, without corresponding peaks in the X-ray diffraction pattern, superimposed on the Mössbauer segregated α-Fe spectrum.

The peaks of the segregated Gd component at the X-ray diffraction are identified with an fcc structure, instead of the expected hcp structure, typical of metallic Gd. This fcc phase has been observed in several metallic rare earths, including Gd, when submitted to high pressures[4].

The NMR measurements in the crystalline compounds showed, in the case of $GdCo_2$, a single resonance line corresponding to the $^{59}$Co line centered at about 61.6 MHz. This is in agreement with other results in the literature[5].

For crystalline $GdFe_2$ we observed two narrow lines centered at 56.6 and 74.4 MHz. The ratio of these frequencies coincides with the ratio of the gyromagnetic factors of the $^{155}$Gd and $^{157}$Gd isotopes[6]. These frequencies correspond to a hyperfine field of about 43.4 T, that is about 4% lower than earlier results[6]. It is possible to identify the quadrupolar interaction transitions through the satellite lines at the positions 55.4, 57.9, 73.1 and 75.0 MHz. The $^{57}$Fe NMR of the $GdFe_2$ compound was also measured, and we can distinguish more than one line.

We will now discuss the milled $GdFe_2$ samples. The first 30 minutes of milling of $GdFe_2$ have not introduced any detectable disorder in the crystalline lattice, or disorder of chemical type, judging from the X-Ray spectra, and from the NMR measurements.

After one hour of milling we can identify in the X-Ray spectrum lines arising from segregation: these lines correspond to α-Fe and to the formation of a phase with lattice parameter around 4.98 Å (assuming a cubic structure). This value of the parameter was computed through a computer program that indexes the X-Ray lines. In the NMR spectra we observe the formation of lines in positions displaced towards lower frequencies respective to those of the original compound. The fact that these lines appear at the left (lower frequencies) shows that the displacement occurs in the direction of the hf fields corresponding to metallic Gd[7]. This may be interpreted as the formation of a phase richer in gadolinium.

Attenuation of the radiofrequency (RF) power by 15 dB did not affect much the width of the line of the original compound. This probably results from the fact that this signal arises from domain walls. The signal from the new phase, on the other hand, decreases for this power level. This is the opposite of the trend observed in the X-Ray spectra. This suggests that the new phase may have less defects, consisting of a crystalline solid solution.

After 3h of milling we still observe the presence of two phases; the width of the line of the original compound broadens. The NMR signal is weaker, and longer measuring times are required to obtain reasonable statistics. The signal around 62 MHz is attributed to a peak in the gain of the measuring coil. The spectra of the samples measured for periods of up to 3 h are shown in Fig. 1 for $^{155}$Gd.

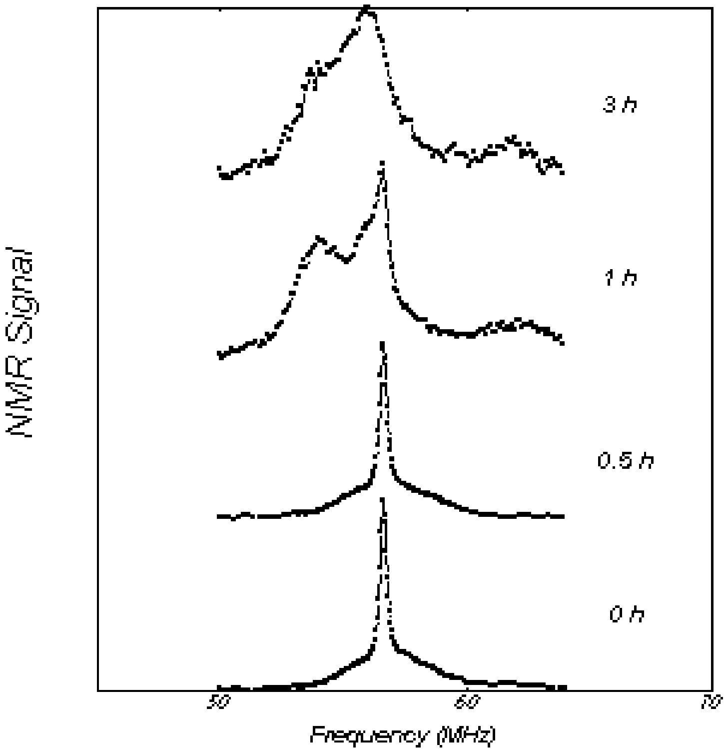

Figure 1 - $^{155}$Gd NMR spectra for the milled $GdFe_2$ samples, at 4.2 K.

After 7 h of milling, new environments richer in gadolinium appear for the Gd NMR probes. The spectra for these samples present large fluctuations due to a very dramatic fall in signal intensity. To be able to analyze them we smoothed the spectra using a moving average, involving three points each time. The smoothed spectra are shown in Fig. 2, compared to the $^{155}$Gd spectrum of the sample milled for 3 h measured with the same RF power (0 dB attenuation).

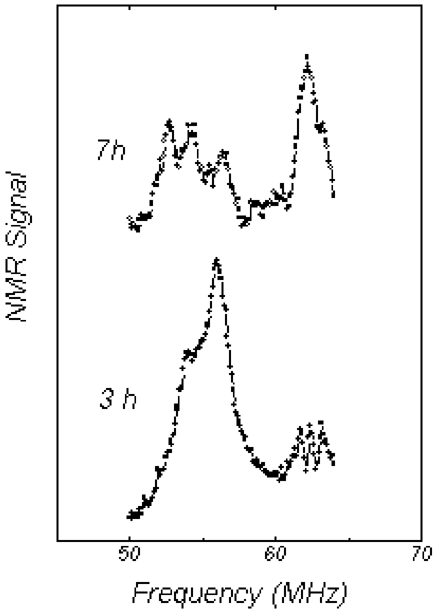

Figure 2 - $^{155}$Gd NMR spectra of the $GdFe_2$ samples milled for 3 and 7 hours, at 4.2 K (0 dB RF attenuation).

The $^{57}$Fe line was followed only up to one hour of milling, due to its low intensity; its center was observed around 32.1 MHz.

Due to the segregation of iron, a line corresponding to metallic Fe was also observed around 46.6 MHz, with a large width of 0.4 MHz. This line broadens with increasing milling time, but maintains constant its intensity relative to the Gd lines.

Concerning the $GdCo_2$ samples, we observed a broadening of the line even for the first minutes of milling, in contrast to the corresponding X-Ray spectra, that show alterations only after 3 h of milling. This may be an indication that a solid solution is formed, such that the Bravais lattice presents no distortions. The baricenter of the line is displaced towards the higher frequencies, probably due to the increase in the cobalt moment known to occur in a-$GdCo_2$[8]. After 5 h of milling the X-Ray spectrum shows peaks due to Co in the bcc structure, and lines in the same positions as those found in the Gd-Fe system after one hour of milling. This segregation effect is reflected in the NMR spectrum through the saturation of the displacement of the baricenter of the line as shown in Fig. 3. This is a result of the reduction in the cobalt moment due to the charge transfer from Gd to the 3d shell of the transition metal[9], in a local environment richer in Gd. After 7 h of milling, the baricenter of the line is displaced to lower frequencies; this is shown in Fig. 3 and the spectra in Fig. 4.

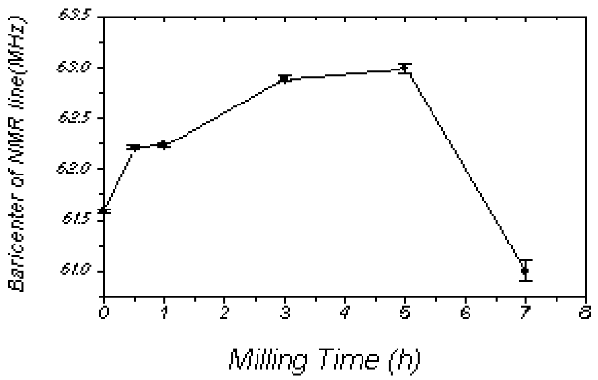

Figure 3 - Displacement of the baricenter of the $^{59}$Co NMR line of the $GdCo_2$ milled samples.

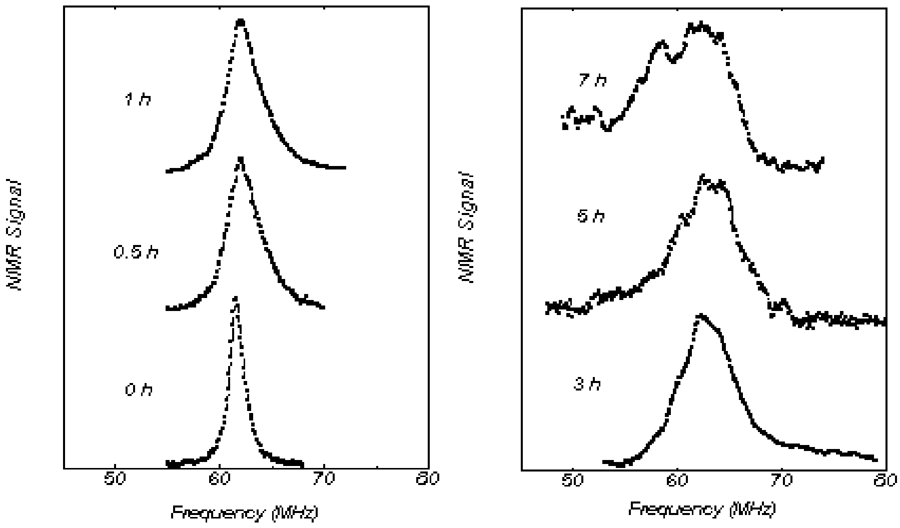

Figure 4 - $^{59}$Co NMR spectra of the $GdCo_2$ samples milled up to 7 h.

After 10 h of milling, the NMR signal is very much reduced, probably due to the decrease in grain size that wipes out signals coming from domain walls, and from the excitation of more defective regions, such as the surface of the grains. The signal from pure cobalt should appear around 217 MHz[10], and is outside the present range of our spectrometer.

## 4. Conclusions

We have used the NMR technique to follow the effects of milling of the intermetallic compounds $GdFe_2$ and $GdCo_2$. New local environments for the Co and Gd atoms were observed with the process of amorphization. The segregation of Fe was also confirmed through the detection of the corresponding NMR lines. The X-Ray spectra were well fitted with lines from pure fcc gadolinium in both compounds. However, the NMR results show that, although the iron and cobalt impurities in the Gd rich matrix do not affect the crystal structure, they significantly affect the hyperfine field, resulting in a value that differs from the field in metallic Gd.

Although the X-Ray spectra do not show the lines corresponding to the original intermetallic compound beyond the point when the segregation sets in, the NMR measurements still show its signature, due to the fact that this technique favors the less defective regions.

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## 6. References

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