

NMR Measurements in Milled GdCo₂ and GdFe₂ Intermetallic Compounds*C.V.B. Tribuzy^{1,3}, A. Biondo², C. Larica², K.M.B. Alves² and A.P. Guimarães¹¹Centro Brasileiro de Pesquisas Físicas, R. Xavier Sigaud 150, 22290-180 Rio de Janeiro, RJ, Brazil²Universidade Federal do Espírito Santo, Departamento de Física, 29060-900 Vitória, ES, Brazil³Present address: PUC/RJ, R. Marquês de S. Vicente 225, 22453-900 Rio de Janeiro, RJ, Brazil

ABSTRACT

We have used the nuclear magnetic resonance technique to study the magnetic and structural properties of the Gd-Co and Gd-Fe metallic systems, starting with the C15 Laves phase intermetallic compounds, and submitting them to a high energy milling process. This leads to the amorphization of the samples, as determined by the X-ray diffraction spectra. For the Gd-Co system the NMR study used the ⁵⁹Co nucleus; in the Gd-Fe system, ^{155,157}Gd and ⁵⁷Fe were used. Both systems showed segregation of the pure elements, after a few hours of milling. In the Gd-Co system, a single line, of increasing width, was observed in the ⁵⁹Co spectrum. In the Gd-Fe system, the ¹⁵⁵Gd and ¹⁵⁷Gd resonances show three lines, arising from electric quadrupole interaction. With increasing milling time, the lines broaden, and extra lines appear attributed to a cubic phase of Gd; this interpretation is supported by the X-ray analysis of the samples. The ⁵⁷Fe NMR spectrum of this system also informs on the direction of magnetization of the samples in the early stages of milling. From 1 h to 7 h of milling, a spectrum of α -Fe was observed. The study of the NMR line intensity as a function of radio frequency (r.f.) power in GdCo₂ suggests the existence of regions of the samples with different degrees of disorder. We have observed the persistence of NMR signals from the original intermetallic compounds in the samples with up to 10 h and 7 h of milling, respectively, for GdCo₂ and GdFe₂.

PACS: 67.80Jd, 75.50.Kj, 71.55.Jv

Keywords: GdFe, GdCo, NMR, amorphization, milling

* To be published in J. Mag. Mag. Mat.

1. INTRODUCTION

The high energy milling method has been used to prepare amorphous, micro- and nano- crystalline materials [1,2]. This is a useful technique for the preparation of materials in the metastable states, and it may supplement other methods, such as melt-spinning, vapor condensation, and sputtering. Solid state reactions induced by severe milling allow the preparation of powder samples of alloys and intermetallic compounds, starting from pure chemical elements. Alternatively, one may obtain amorphous samples by milling, starting from crystalline samples of alloys and compounds prepared conventionally.

The nuclear magnetic resonance (NMR) technique allows the study of magnetic and structural properties of magnetic samples. The hyperfine interactions of the different nuclides give information on the local atomic environments; the intensity of the NMR signal is correlated to the local magnetic anisotropy, and to the number and mobility of the magnetic domain walls (e.g., [3]). This technique has been applied to the study of the pure intermetallic compounds used in the present study [4].

We present here the results of the analysis with NMR of milled Laves phase intermetallic compounds, as a function of the milling time. A preliminary version of the results was given elsewhere [5]. This has allowed the investigation of structural changes of the samples, with increasing degree of disorder.

2. EXPERIMENTAL

The intermetallic compounds GdFe_2 and GdCo_2 crystallize in the cubic Laves phase structure (C15), and order magnetically at 796 K and 403.7 K, respectively [6]. The compounds were prepared by arc melting the pure elements under argon atmosphere. The melted buttons were sealed in evacuated quartz tubes, then annealed during 90 hours at 850 °C and quenched in cold water. The buttons were filed to remove a thin layer from the surface; they were then crushed to obtain the powder for NMR and X-ray diffractometry. The X-ray pattern showed the appropriate crystal structure; the Co K_α line was used in the analysis.

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 $\text{HRc} = 65 \pm 1$), with cylindrical shape, and internal dimensions of 4.0 cm height and 7.2 cm diameter. The milling tool was a massive cylinder of the same material, occupying 43% of the vial internal volume. To prevent air from entering the vial during the milling procedure, the vial was sealed with an 'o' ring, and the top was screwed. Subsequently, the sealed vial was placed in a commercial vibrating frame machine, and during the milling process the vial temperature was kept around 320 K. Samples were collected after various pre-established times and were labeled with the actual milling time.

To collect the samples, the vial was taken from the vibrating machine and opened inside a glove box, filled with argon gas. While under argon atmosphere, the

collected powder was put into a sealed 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 powders, the collected samples were kept at liquid nitrogen temperature when not in use.

The NMR measurements were performed using the zero-field spin echo technique, at 4.2 K. A home-made automated pulse spectrometer was used. The typical pulse sequence consisted of two 0.5 μ s pulses; each NMR spectrum required from 1 to 20 hours of measurement. The NMR spectra were made with resonances from ^{59}Co , ^{57}Fe , ^{155}Gd and ^{157}Gd nuclei. In the present analysis, we have used the gyromagnetic ratios for the nuclei given in reference 4 (Table 1).

Nuclide	Spin	$\gamma/2\pi$ (MHz/T)	Electric Quadrupole Moment (10^{-28} m^2)	Isotopic Abundance (%)
^{155}Gd	3/2	1.307	1.59	14.73
^{157}Gd	3/2	1.713	1.69	15.68
^{59}Co	7/2	10.054	0.42	100
^{57}Fe	1/2	1.3756	---	2.2

Table 1. Nuclear parameters of the nuclides used in the present study.

3. RESULTS AND DISCUSSION

For the Gd-Co samples the resonance was studied at the ^{59}Co nucleus, and for the Gd-Fe samples, the resonance was observed at both atomic sites, Gd and Fe. A study of the NMR signal intensity with the r.f. field amplitude was also made, supplying information on some effects associated with the reduction in grain size and increase in the number of defects with increasing milling time.

3.1 Gd-Co

The X-ray spectra (Fig. 1) of the milled samples show broadening of the lines, starting from 3 h of milling. For the 5 h milled sample, a new structure seems to be formed, verified by the presence of lines around the positions $2\theta = 36^\circ, 42^\circ, 52^\circ, 61^\circ, 73^\circ$ and 77° . With the exception of the line positioned around 52° , ascribed to cubic cobalt metal, every new line corresponds exactly to an fcc Gd structure, with a lattice parameter equal to 4.96 Å. This value is in agreement with that found for an fcc Gd structure, obtained from the milled stable hcp Gd structure [1]. Therefore, this is evidence that segregation of the initial elements has occurred. This effect had already been observed by some authors in the YFe_2 isostructural compound submitted to mechanical milling [2]; we had not found this effect in this same compound [7].

As the milling time increases, the X-ray lines corresponding to the initial compound disappear. The new lines broaden, and after 100 h two very broad lines remain, the breadth arising from the strong reduction in grain size of fcc Gd and fcc Co.

The NMR spectrum of the ^{59}Co nucleus in the crystalline compound GdCo_2 presents a single line centered at 61.6 MHz, which corresponds to a hyperfine field of 6.13 T. The fact that there is only one line indicates that all Co atoms are equivalent, both crystallographically and magnetically. This spectrum is in general agreement with the early work of Hirosawa and Nakamura [8] and with later results [9].

With the milling process, the NMR line broadens because of the distribution of hyperfine fields, and to a smaller extent, to an electric field gradient distribution. The chemical or topological disorder leads to a distribution of magnetic moments at the transition metal site. The corresponding NMR spectra are shown in Fig. 2.

The broadening of the ^{59}Co NMR lines is noticeable in the spectra of the milled samples starting from 30 min, differently from what is observed in the X-ray spectra. This result shows that the first 1 h of milling of GdCo_2 has introduced chemical disorder, while preserving the crystalline lattice.

One determines the baricenter of the NMR line by least squares fitting the spectra with a single lorentzian line. This baricenter moves toward higher frequencies, as a function of the milling time, for times up to 3 h. This behavior is interpreted as resulting from the increase in Co moment associated with the smaller density in the disordered state, leading to a higher degree of localization of the 3d moment; this effect had been previously observed in amorphous $\text{Gd}_{0.33}\text{Co}_{0.67}$ films [10]. After 7 h of milling, the baricenter of the NMR lines is displaced toward lower frequencies, due to the presence of a resolved line positioned around 57.8 MHz. This line is attributed to some Co impurity atoms within the fcc Gd matrix, after the occurrence of segregation. The value of the associated hyperfine field, 5.75 T, is very near to that calculated for Co as diluted impurity in a Gd host [11].

As the milling time increases, there is a strong reduction of the NMR signal intensity, as the hyperfine field distribution becomes broader, and the contribution of the domain walls is decreased (see below). For this reason, we could not follow the NMR signal beyond 10 h of milling.

The dependence of the spin-echo intensity on the r.f. field amplitude (related to the r.f. power level) was examined in order to study the behavior of regions in the sample presenting different magneto-crystalline anisotropy, as a function of the milling time. This type of information can be obtained, as the actual r.f. field amplitude that is felt by the nucleus depends on the magnetic anisotropy field acting on the atomic moment. Since the NMR signal intensity is related to the latter field, studies of signal intensity versus r.f. field are informative on the local magnetic anisotropies.

The dependence of the spin-echo intensity (I) on the r.f. field amplitude B_1 in crystalline GdCo_2 was interpreted according to a model [9] that includes contributions of magnetic domains and domain walls. For this sample, in the region of the I versus B_1 curve with $B_1/B_1^{\text{max}} \leq 0.4$, the NMR signal comes mostly from domain walls, and for $B_1/B_1^{\text{max}} > 0.4$, (for our values of B_1^{max}) it comes mostly from domains. Based on this model, the dependence of the echo height on the r.f. field amplitude in the milled samples shows the decrease of the domain wall contribution, associated with grain size reduction, as the milling time increases. This is shown in Fig. 3.

The above results were obtained for the ^{59}Co resonance line in the neighborhood of the line position for the GdCo_2 intermetallic compound. We did not search for the signal coming from metallic Co, whose presence was identified in the X-ray spectra, because its resonance, around 216 MHz [12], is presently outside the scope of our spectrometer.

3.2 Gd-Fe

After 1 h of milling, the X-ray spectrum of GdFe_2 shows strong new lines positioned around $2\theta=36^\circ, 42^\circ, 45^\circ, 49^\circ, 52^\circ, 61^\circ, 73^\circ$ and 77° , among weak lines of the original compound (Fig. 1). After 3 h of milling the lines of the GdFe_2 compound disappear, the new lines remaining, with the exception of those lines around 45° and 49° . These two lines were attributed to the presence of GdFeO_3 , formed in the 1 h sample, during its manipulation in the glove box. Comparing the X-ray line positions for GdFe_2 milled for 3 h to those for GdCo_2 milled for 5 h, we find good agreement. The line around 52° for the Gd-Fe series was attributed to bcc Fe and the other lines to fcc Gd structure, with a lattice parameter equal to 4.98 Å [13]. We conclude that segregation also took place in this system.

For long milling times the X-ray spectrum consists of two broad lines around 36° and 52° , corresponding to much reduced grains of fcc Gd and bcc Fe phases, respectively.

The GdFe_2 NMR spectra of the ^{155}Gd and ^{157}Gd nuclides show lines at 56.64 MHz and 74.36 MHz, respectively; these frequencies are in the ratio of the $^{155, 157}\text{Gd}$ gyromagnetic ratios [4]. The average hyperfine field, computed for the two nuclides, is 43.37 T. We observed satellite lines due to quadrupolar interaction in the spectra of both nuclides, with a peak-to-peak distance of 2 MHz. In spite of the high symmetry of the Gd site, and of the fact that a Gd^{3+} ion has zero orbital angular momentum, we observe an electric quadrupolar interaction. The explanation for this interaction lies in relativistic effects at the 4f shell, small effects of magnetostriction, and induction of an electric field gradient due to non-s conduction electrons at the Gd site [14].

After the first 30 minutes of milling, there were no changes in the NMR lines of GdFe_2 . No significant degree of disorder was introduced in the crystalline lattice, up to this time, and this is in agreement with the behavior of the lines in the X-ray spectra. After 1h of milling, the NMR lines becomes broader.

In a disordered solid, the magnetic moment distribution for the rare earth atom is narrower than that of transition atoms, because of the shielding of the 4f shell [15]. The broadening of the NMR lines for Gd in GdFe_2 is due to the distribution of transferred hf fields from the Fe atoms, and to the electric field gradient distribution. The $^{155, 157}\text{Gd}$ NMR spectra of GdFe_2 samples milled for 1 h show new lines at 54.2 MHz and 72.1 MHz, corresponding to an average hf field of 41.8 T. This value is higher compared to the hf field for pure hcp Gd, of about 37 T [16]. This higher hyperfine field may be partly due to the presence of Fe atom impurities in the new fcc Gd phase, precipitated after 1 h of milling.

After one hour of milling, the $^{155, 157}\text{Gd}$ NMR lines belonging to the original GdFe_2 compound are still intense, while in the X-ray spectrum the GdFe_2 lines present very low intensity. This is probably due to the fact that the new phase precipitates in smaller grains, and NMR signals from these are relatively more difficult to observe, as opposed to the regions of higher degree of local order, of relatively unmodified GdFe_2 . The possibility that these new lines belong to oxide was ruled out, since Gd hyperfine fields in GdFeO_3 are found to be very low, around 6 T [17], and Gd oxide is paramagnetic.

As the milling time increases, the Gd NMR signal intensity decreases, because of the broadening of the hyperfine field distribution, and the smaller mobility of the domain walls, with the introduction of defects. The Gd signal in this system was accompanied for up to 7 h of milling. The ^{155}Gd and ^{157}Gd spectra are shown in Fig. 4.

The verification of the segregation effect in the NMR spectra was also done through the ^{57}Fe resonance, in the metallic Fe resonance region. The observed linewidth is larger than that of the crystalline bcc Fe, and the line exhibits also an asymmetry. These features may be the result of the presence of an fcc Fe phase, or to disordered metallic Fe. The corresponding NMR spectra as a function of milling time are shown in Fig. 5.

The ^{57}Fe NMR spectra in the resonance region of this nucleus in the original GdFe_2 intermetallic compound show three lines (Fig. 6). The ^{57}Fe nuclear spin is $1/2$, and therefore, there is no quadrupolar interaction. The three lines are attributed to magnetically non-equivalent Fe sites, arising from the fact that the direction of magnetization of GdFe_2 is in the $(1\bar{1}0)$ plane [18]. Before milling the line positions are 31.35 MHz, 33.46 MHz and 35.50 MHz; using the nuclear g-factor given by Dormann [4] one obtains hyperfine fields of 22.94 T, 24.33 T and 25.81 T. Following the procedure of Genin et al. [18] and using these line positions, a value of $\psi=77^\circ$ is derived for the angle of the Fe magnetic moment with the [001] direction; this should be compared to $\psi=61^\circ$ obtained with Mössbauer spectroscopy by these authors. The angle determined by NMR applies to the regions where the signals come from: if the signals originate in domain wall centers, the angle will not be necessarily the same as in the domains, and this may explain the disagreement. The persistence of these lines, for samples with up to 30 minutes of milling, confirms the conclusion that no significant disorder was introduced until that moment. For 1 h of milling this signal is very reduced and the NMR spectrum presents a large statistical dispersion. The fall in signal intensity for this nucleus was very critical, since the ^{57}Fe isotopic abundance is only 2.2%. This makes this signal intensity naturally lower than that of the Gd signal, whose isotopic abundance is around 15% for each isotope.

4. CONCLUSIONS

We have applied the pulsed NMR technique to study the hyperfine and structural modifications, as function of milling time, of the GdCo_2 and GdFe_2 crystalline intermetallic compounds. The X-ray diffraction had also been applied to the structural study of GdCo_2 .

Mechanical milling introduces elastic instabilities in the crystalline lattice, with grain fracture, chemical and topological disorder. This leads to broader lines in the X-ray spectra. The milling of the GdCo_2 and GdFe_2 compounds induced segregation of the initial compound constituents. In both systems, after 5 h of milling of the first, and 1 h of the second, we observed the formation of a metallic Gd phase, with an fcc structure, together with fcc Co in the Gd-Co system, and bcc Fe in the Gd-Fe system. These phases were identified from the X-ray spectra line positions.

Through the nuclear magnetic resonance of ^{59}Co in GdCo_2 we could verify the introduction of chemical disorder up to the first hour of milling. The ^{59}Co NMR line broadening is due to the distribution of Co hf fields (and magnetic moments), and to

the electric field gradient distribution. The NMR signal drops significantly as the milling time increases. We were able to accompany this signal up to 10 h of milling.

The dependence of the NMR signal intensity on r.f. power level in the Gd-Co system reflected the fall in the number of domain walls, due to the reduction in grain size, or decrease in mobility, with the increase in the density of defects.

Through the resonance of ^{155}Gd , ^{157}Gd and ^{57}Fe , we have verified that the first 30 minutes of milling of GdFe_2 did not introduce any significant type of disorder in the original crystalline lattice. Above 1 h of milling, the broadening of the $^{155, 157}\text{Gd}$ lines is due to the transferred hyperfine field distribution, but also to the pinning of domain walls, because of the introduction of defects.

Segregation was identified in both systems, through the ^{59}Co , ^{155}Gd and ^{157}Gd NMR lines. The extra lines in the spectra, which arise from this effect, reveal the existence of an fcc Gd phase, with transition metal impurities. Segregation was also verified through the NMR line of metallic Fe, which appears above 1 h of milling.

We could still observe the lines belonging to the original compounds, even after the onset of segregation. This is probably related to the fact that the NMR technique privileges signals coming from more locally ordered regions, in detriment of the lines coming from reduced grains, which is the case of the precipitated new Gd phase.

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FIGURE CAPTIONS

Figure 1- X-ray diffraction patterns a) of the GdCo_2 milled samples, and b) of the GdFe_2 milled samples.

Figure 2- ^{59}Co NMR spectra of the GdCo_2 milled samples.

Figure 3- Dependence of the NMR signal intensity versus relative r.f. power, for different milling times in the GdCo_2 samples.

Figure 4- ^{155}Gd (a) and ^{157}Gd (b) NMR spectra of the GdFe_2 milled samples.

Figure 5- ^{57}Fe NMR spectra in the metallic Fe resonance region. All the spectra are normalized by the Gd signal around 56 MHz.

Figure 6- NMR spectra in the ^{57}Fe resonance region in the GdFe_2 compound milled up to 1 h. The three lines arise from the fact that the Fe sites are magnetically non-equivalent.

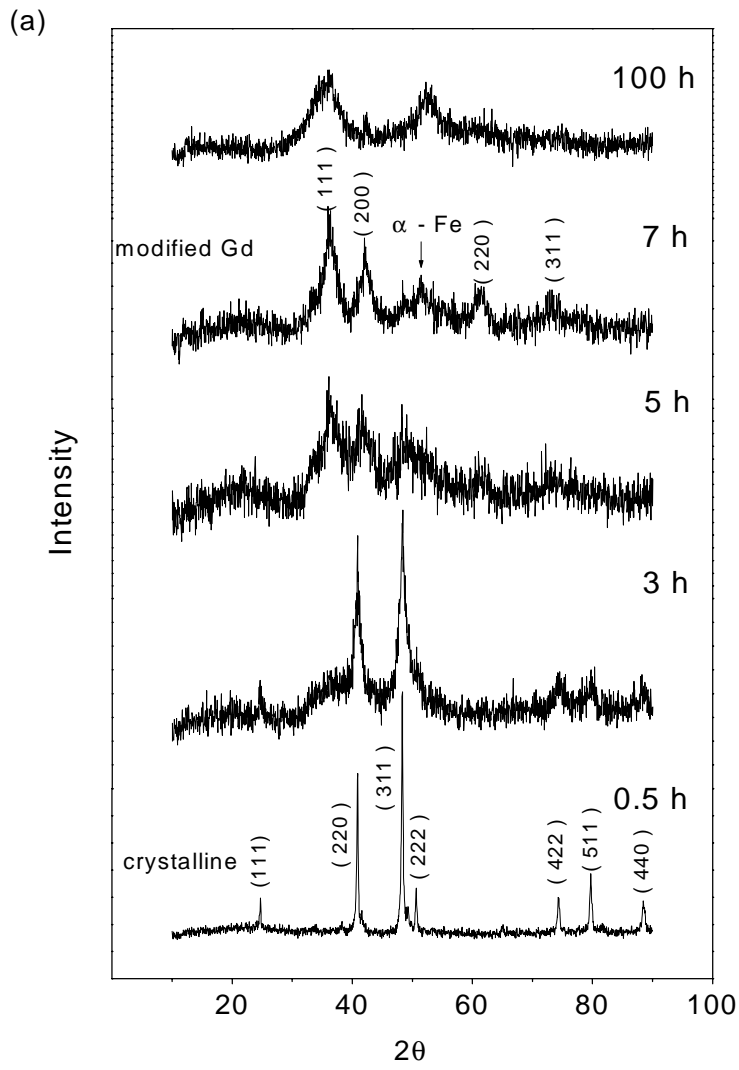


Figure 1(a)

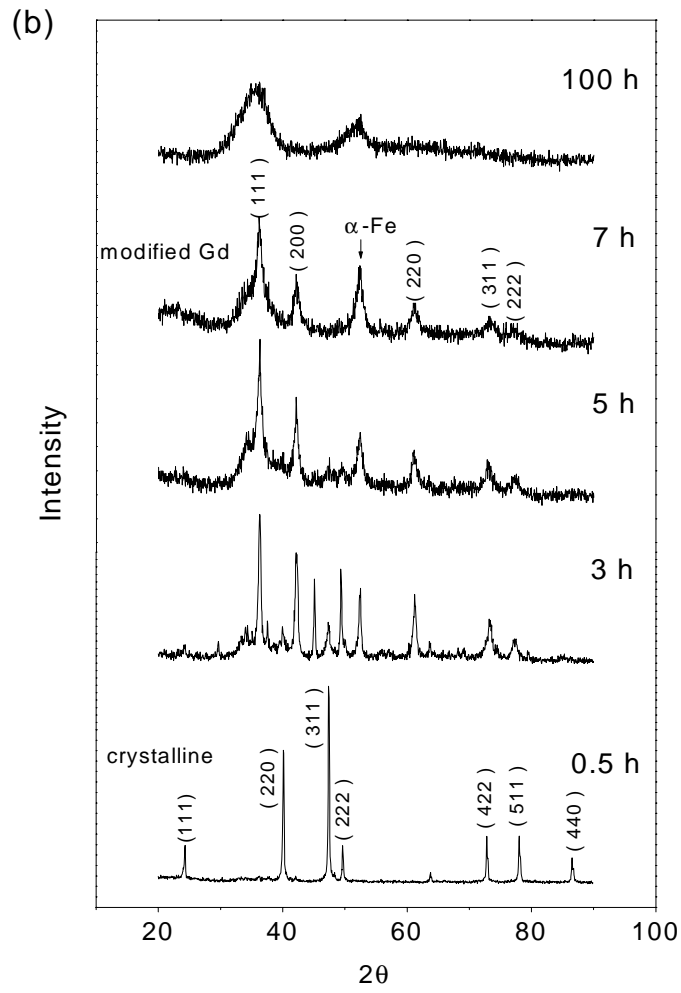


Figure 1(b)

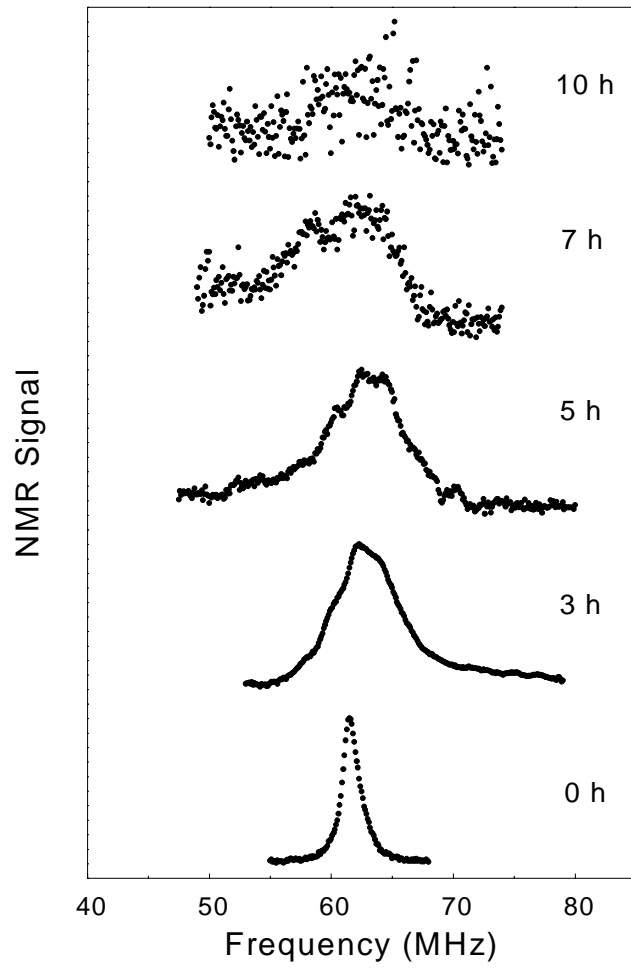


Figure 2

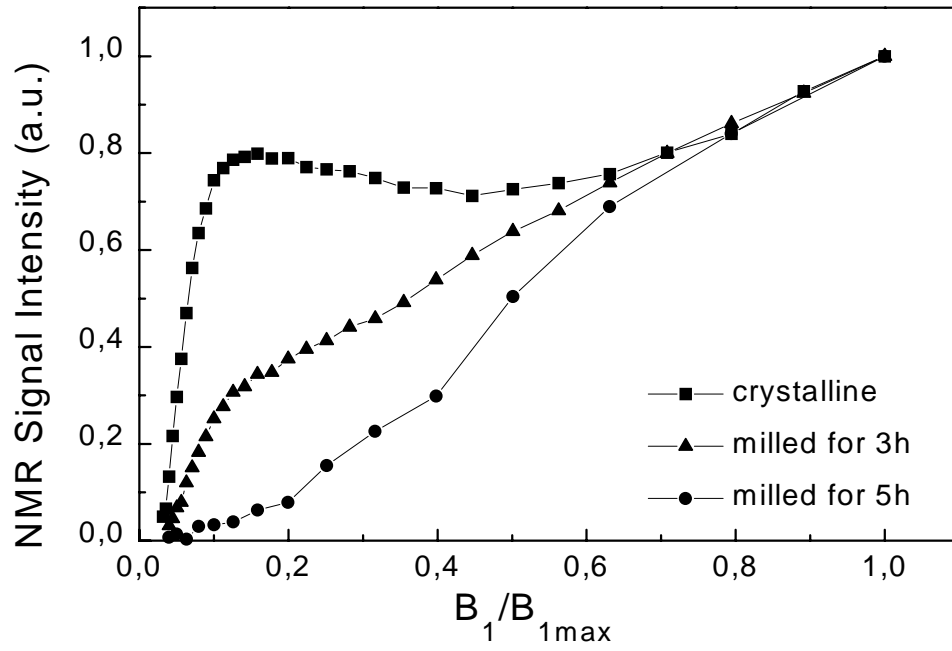


Figure 3

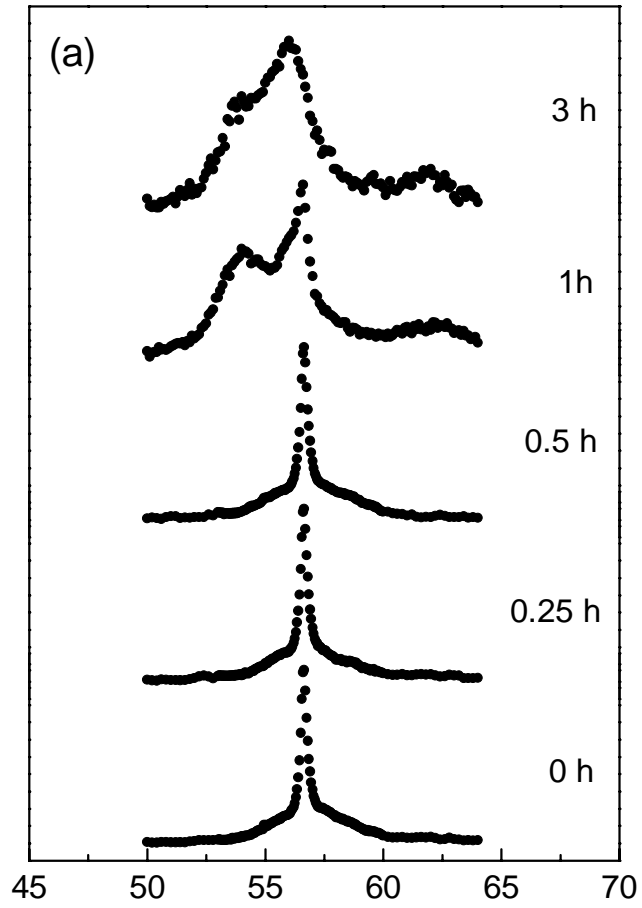


Figure 4(a)

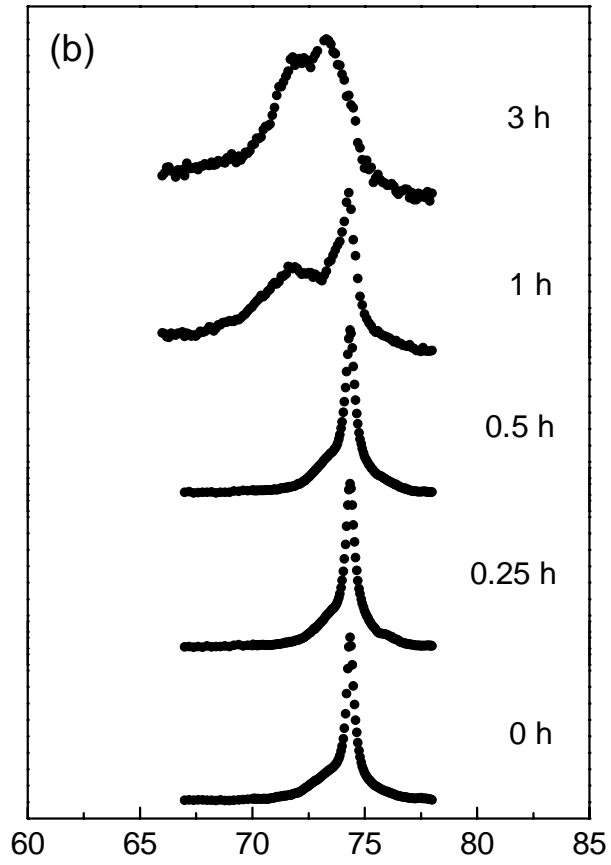


Figure 4(b)

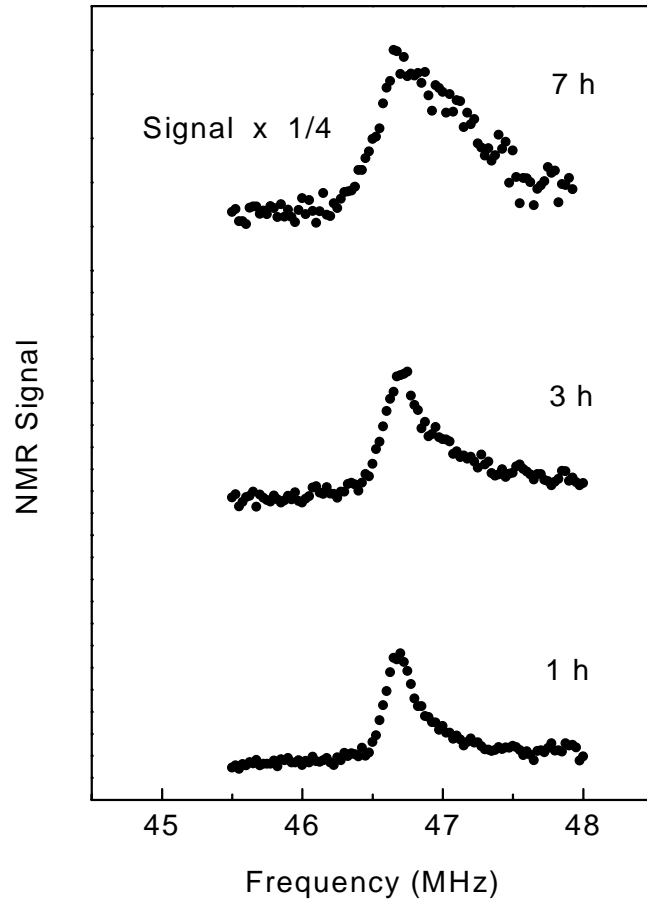


Figure 5

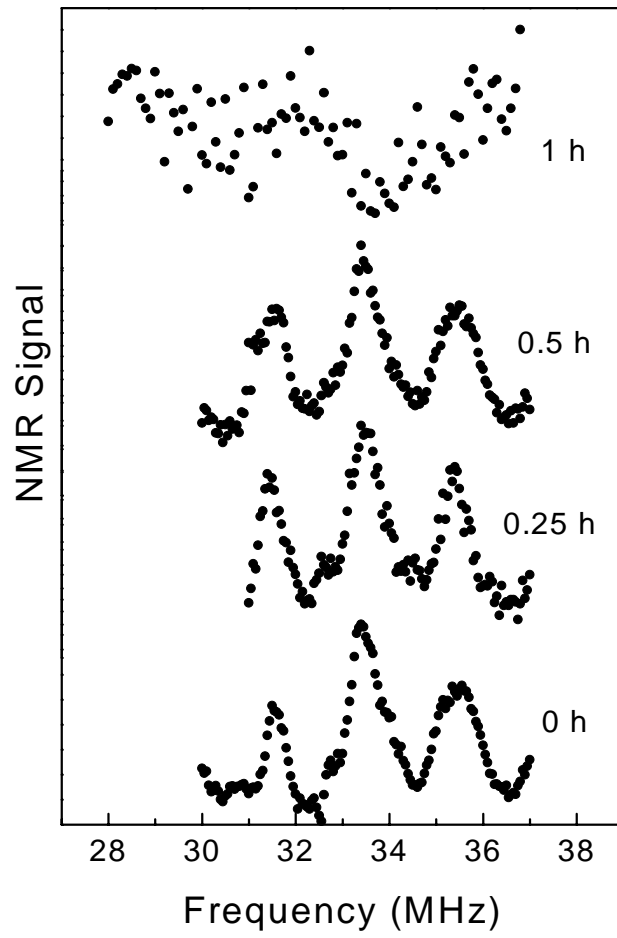


Figure 6