Nuclear Magnetic Resonance Studies of Martensitic Phase Transformation in Ni–Ti Shape Memory Alloys

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Ni–Ti Shape Memory Alloys (SMA) are of great technological interest because they have the best shape memory behaviour of all SMA. Moreover, Ni–Ti thin films are considered to be one of the most promising solutions for the development of new micro actuators. In order to use Ni–Ti in the thin film-state, it is therefore important to know if the properties of the martensitic phase transformation responsible for the shape memory effect are different in Ni–Ti thin films and in bulk materials. For that purpose, 61Ni Nuclear Magnetic Resonance (NMR) measurements have been performed at very high magnetic field (14 T) in Ni–Ti bulk alloys as well as in thin films. The process of nucleation and growth of the R-phase and of the martensite in the different samples have been studied by means of a careful analysis of the 61Ni NMR spectra recorded at different temperatures from \( T > R \) to \( T < M_f \). The complex structure of the NMR spectra during phase transformation has been interpreted as a sum of contributions arising from the coexisting crystalline phases. The spectral deconvolution is very difficult to achieve because the NMR martensitic line of complex shape is partly superimposed on the austenitic line. However, additional NMR measurements in a 61Ni enriched Ni–Ti bulk alloy allowed us to identify the microscopic interactions responsible for the martensitic line shape. With the help of this analysis it was then possible to determine the volume fraction of the different phases present at each temperature in the Ni–Ti bulk alloys and thin films. The NMR results showed that in Ni–Ti bulk alloys, where the R-phase transformation does not take place or is only partial, the martensitic transformation is not complete even at temperatures well below \( M_f \) as determined by calorimetry. On the other hand, in thin films showing a well distinct two-step transformation via the R-phase no remaining austenite could be detected below the \( R_f \) temperature.

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1. Introduction

The shape memory effect and the superelasticity are remarkable mechanical properties that occur in association with a thermoelastic Martensitic Phase Transformation (MPT) from a high-temperature parent phase called austenite (A) to a low-temperature phase called martensite (M). Among all Shape Memory Alloys (SMA), the intermetallic compound Ni–Ti is one of the most interesting for its applications. Its popularity is due to its excellent shape memory properties, including strong shape recovery forces and low fatigue. Moreover, the biocompatibility of Ni–Ti makes it the only SMA suitable for implantation in human bodies. The MPT in Ni–Ti transforms generally a cubic austenite with a B2 structure into a monoclinic martensite with a B19′ structure. Depending on the composition and on the thermomechanical treatment an intermediate rhombohedral phase, called R-phase, may be observed.

Thin films of shape memory alloys and especially of Ni–Ti are considered to be one of the most promising solution for the development of new micro actuators required for many applications in the field of micro systems technology. The fact that the Ni–Ti films of a thickness of only a few microns still show a memory effect allows their integration in MEMS and increases the frequency of consecutive actuation. Furthermore, miniaturised SMA devices have the highest specific work power value in comparison with other type of actuators. However it has been reported that the features of the MPT in SMA thin films depend on the film thickness. In order to use Ni–Ti in the thin film-state, it is therefore important to know, from both a fundamental and a technological point of view, if the properties of the MPT in Ni–Ti thin films differ from those observed in bulk materials and if a size effect occurs.

Nuclear Magnetic Resonance (NMR) has proved to be a powerful method to investigate the behaviour of the MPT in shape memory alloys such as Cu–Zn–Al, Ni–Al and Ag–Cd. The NMR absorption spectrum is sensitive to the local environment surrounding the given atom. If the crystallographic and/or electronic structure change(s) during the MPT, it is possible to detect the transformation and acquire information about the different phases by measuring the NMR parameters of the line. This technique provides some unique information about the process of nucleation and growth of the martensite in the parent phase matrix.

Despite its great technological interest, no NMR measurements have been performed on Ni–Ti beside those made within the frame of our work. This is probably due to the difficulties associated with the nuclear properties of 61Ni, 47Ti, and 49Ti, which are the only non-zero spin isotopes that can be used as NMR probes in Ni–Ti. As a matter of fact, 47Ti \( (I = 5/2) \) and 49Ti \( (I = 7/2) \) exhibit large quadrupole couplings leading to a dramatic broadening of the NMR lines in positions of non-cubic symmetry. Therefore, the Ti isotopes cannot be used as NMR probes. The 61Ni \( (I = 3/2) \) could be a good candidate for NMR experiments but its natural abundance is very poor (1.19%). Two solutions can be used to enhance the 61Ni NMR signal: the isotopic enrichment of the samples or the application of a very strong static magnetic field.

In the present work, 61Ni NMR measurements have been performed at very high magnetic field (14 T) in Ni–Ti enriched and non-enriched bulk alloys as well as in thin films. The growth process of the R-phase and the martensite have
been studied in the different samples and a special attention has been paid to the differences that may appear between bulk alloys and thin films. For a better understanding of the results presented in this paper the physical significance of the main NMR parameters is briefly summarized in Appendix A.

2. Experimental Details

The Ni–Ti laminated wires used in the present experiment had a cross-section of 0.06 × 0.75 mm and their chemical composition was determined to be Ti–50.6 at%Ni by energy-dispersive X-ray spectroscopy (EDS) in a Philips XL30 Scanning Electron Microscope (SEM). Samples for NMR measurements were prepared by cutting the wires into 3–5 mm long pieces, which were subsequently annealed at 873 K for 30 min in a quartz capsule and water quenched at room temperature.

The Ni–Ti thin films were deposited in the Institute of Applied Physics at EPFL by rf magnetron sputtering on unheated rotating glass substrates at a temperature estimated to be approximately 450 K due to the sputtering process. Two identical targets of equiatomic Ni–Ti alloy had to be enriched with some pure Ti dots to compensate for the titanium deficiency usually observed in thin films prepared by this technique. A rf sputtering power of 120 W was used with a working gas of argon at a pressure of 0.667 Pa. Typical film thickness ranges from 7 to 9 µm. The composition of the films was determined to be Ni–50.5 at%Ti by EDS. The amorphous as-deposited foils were peeled from the substrates and annealed in a quartz-tube at 873 K for 30 min and then water quenched.

A 61Ni enriched Ni–Ti alloy was elaborated in the Structural Metallurgy Laboratory of the “Ecole Nationale Supérieure de Chimie” in Paris. Weighted amounts of Ni and Ti commercial alloys and high-purity 61Ni powder were melted by high frequency induction heating in a quartz tube in Argon atmosphere. The NMR sample was then prepared by spark cutting the ingot into slices of 120 µm thickness that were subsequently annealed at 873 K for 30 min in a quartz capsule and water quenched at room temperature.

Before the beginning of the NMR measurements each sample has been thermally cycled twenty times to stabilize the transformation temperatures and the hysteresis loop. Differential Scanning Calorimetry (DSC) measurements have been performed after the treatment. They indicated that both the wires and the thin films undergo a two-stage transformation A → R-phase → M on cooling, while the R-phase transformation does not occur in the 61Ni enriched Ni–Ti sample, which transforms directly from austenite into martensite. The transformation temperatures of the different phases are reported in Table 1. It has to be noted that for the Ni–Ti wires the temperatures \( T_r \) and \( T_f \) could not be determined accurately because the DSC peaks associated with the A → R phase and R-phase → M transformations are superimposed. The transformation temperatures indicated in Table 1 for this sample have therefore been evaluated by the tangent method.

The NMR measurements were carried out with a home-built spectrometer in a 14 T Oxford superconducting magnet with a 50 mm diameter variable-temperature (4–330 K) bore. Standard pulse NMR techniques were applied for 61Ni absorption spectra acquisition. Due to the limited spectral range of the rf wave, a point by point reconstruction technique had to be performed in order to measure the broad 61Ni line. Each point on the spectrum represents the measured area under the spin echo for the corresponding irradiation frequency. All the measurements were carried out at constant equilibrium temperature during the cooling of the samples.

3. Results and Discussion

3.1 Bulk specimens

3.1.1 Ni–Ti wires

In order to test the NMR technique in Ni–Ti alloys using 61Ni nuclei as microscopic probes and to establish references, NMR measurements have first been performed in Ni–Ti wires, which can be considered as a bulk specimen.

Before being able to determine the volume fraction of the different phases present at a given temperature during the transformation it is necessary to study the NMR spectral parameters, such as the linewidth and the resonance frequency, of each phase as a function of temperature. Figure 1 shows the 61Ni NMR spectrum obtained at \( B_0 = 14 \text{T} \) in the austenitic phase (\( T > T_r \)). It is composed of a narrow central line of Gaussian shape superimposed on a broad distribution of satellite transitions resulting from first order quadrupole interactions in an imperfectly cubic alloy. The width of the line (about 20 kHz) is temperature independent. The resonance frequency seems to increase very slightly as the temperature decreases (increase of about 0.5 kHz for a decrease of temperature of 10 K). However, the temperature range which could be investigated before the sample transforms into R-phase is small (about 30 K), and the variation is so weak that it can be included in the experimental error.

The R-phase → M transformation starting before the end of the A → R-phase transformation, it is not possible to record a NMR spectrum arising only from the R-phase. The
linewidth and the resonance frequency of this phase were obtained through deconvolution of the NMR spectra measured at temperatures included between \( R_s \) and \( M_s \). The contribution of the austenite was subtracted from the total spectrum by fixing its spectral parameters at a given temperature on the basis of the measurements made at temperatures above \( R_s \). It was found that the R-phase resonance frequency decreases while its linewidth increases as the temperature is lowered.

Figure 2 shows a \( ^{61}\text{Ni} \) NMR spectrum recorded at \( B_0 = 14 \text{T} \) and at a temperature well below \( M_f \) as determined by DSC. This spectrum is no longer symmetric but shows a shoulder at higher frequency. To determine the origin of the spectral shape, measurements of the NMR spectra were performed at lower external magnetic field (\( B_0 = 8 \text{T} \)). Unfortunately the signal to noise ratio was so low and the spectrum so wide that it was not possible to distinguish the two components of the spectrum any more. Nevertheless, the results showed that the total width of the line is inversely proportional to \( B_0 \). The strong broadening of the \( ^{61}\text{Ni} \) NMR spectra observed in the martensitic phase seems therefore to originate from second order quadrupolar interactions. \( ^{61}\text{Ni} \) having a spin 3/2, a non-zero quadrupolar moment and the symmetry of the martensite being no more cubic but monoclinic, such interactions may drastically change the shape of the NMR spectra. However, since the two peaks are not resolved at \( B_0 = 8 \text{T} \), it is not possible to determine if the space between the two components of the spectral doublet is proportional to \( 1/B_0 \) or if the width of only one NMR line shows this feature, covering the second line at lower magnetic field.

Two hypothesis are therefore possible: the first one is that the NMR martensitic line is broadened by second order quadrupolar interactions but the two components are not resolved at \( B_0 = 14 \text{T} \). The shoulder comes then from a fraction of austenite, which remains untransformed even at very low temperature. The resonance frequency of the shoulder corresponds effectively to that of the austenitic line at this temperature. Such observations have already been made in Ag–Cd SMA where Scherrer\(^6\) has shown that 7% of austenite were still present at a temperature far below \( M_f \). The second hypothesis is that the line doublet observed at \( B_0 = 14 \text{T} \) corresponds to the splitting by second order quadrupole interactions of the martensitic line in two distinct components.

To answer this question a Ni–Ti alloy with a 10% enrichment in \( ^{61}\text{Ni} \) was elaborated. With such a sample the signal to noise ratio at lower magnetic field is much higher, and the different components can be distinguished.

### 3.1.2 \( ^{61}\text{Ni} \) enriched Ni–Ti Alloy

The \( ^{61}\text{Ni} \) NMR spectra obtained in the \( ^{61}\text{Ni} \) enriched sample at \( T = 255 \text{K} \) (i.e. 77 K below \( M_f \) as determined by calorimetry) in external magnetic fields of 14 T and 8 T are shown in Figs. 3 and 4 respectively. At \( B_0 = 14 \text{T} \), the shape of the NMR spectrum is similar to that observed in the Ni–Ti wires: it is also composed of two partially resolved NMR lines. However the spectrum measured at the same temperature but at \( B_0 = 8 \text{T} \) shows not only two but three partly resolved peaks. The origin of the different components could be determined by studying the spacing between the three different lines. It thus appeared that the two components located on each side of the spectrum measured at \( B_0 = 8 \text{T} \) (labelled “1” and “3” in Fig. 4) constitute the partly resolved doublet of the martensitic line split by second order quadrupolar interactions. As a matter of fact, this two maxima are separated by \( 110 \pm 5 \text{kHz} \) at \( B_0 = 8 \text{T} \), while the two lines “A” and “B” observed on the spectrum measured at \( B_0 = 14 \text{T} \) (see Fig. 3) are separated by \( 70 \pm 5 \text{kHz} \). These results show therefore that the spacing between these two components is inversely proportional to \( B_0 \) within the experimental error.

The resonance frequency (30.77 ± 0.005 kHz) of the central line (peak labelled 2 in Fig. 4) of the spectrum obtained at \( B_0 = 8 \text{T} \) is very near of that of the austenitic line measured at \( B_0 = 8 \text{T} \) and at \( T = 298 \text{K} \) in the Ni–Ti wires.

![Figure 2](image2.png)  \( ^{61}\text{Ni} \) NMR absorption spectrum in Ni–Ti wires at \( T = 86 \text{K} \) and \( B_0 = 14 \text{T} \).

![Figure 3](image3.png)  \( ^{61}\text{Ni} \) NMR absorption spectrum in a \( ^{61}\text{Ni} \) enriched Ni–Ti alloy at \( T = 255 \text{K} \) and \( B_0 = 14 \text{T} \).

![Figure 4](image4.png)  \( ^{61}\text{Ni} \) NMR absorption spectrum in a \( ^{61}\text{Ni} \) enriched Ni–Ti alloy at \( T = 255 \text{K} \) and \( B_0 = 8 \text{T} \).
(30.775 ± 0.0025 kHz). The resonance frequency of the austenitic line being almost independent of temperature, it can be concluded that the peak labelled “2” observed at \( B_0 = 8 \) T in the \(^{61}\)Ni enriched Ni–Ti sample arises from a fraction of austenite, which is still not transformed even at a temperature well below \( M_s \) as determined by calorimetry.

These results are in accordance with both hypothesis made above and not only with the first one as proposed in our previous publications.

It is very difficult to evaluate precisely the volume fraction of the retained austenite at \( T = 255 \) K in the \(^{61}\)Ni enriched Ni–Ti alloy. The transformation temperatures of this alloy being very high and located above the limits of the experimental device, it was not possible to determine the spectral parameters of the austenitic phase in this alloy. Moreover the pronounced asymmetry of the spectrum obtained at \( B_0 = 8 \) T does not allow fitting the NMR martensitic line with a sum of two gaussians. A rough evaluation shows that at least 7% of austenite are still present at a so low temperature. It has to be noted that even though this value is only approximative, the NMR measurements clearly show that this fraction in not negligible.

### 3.1.3 Following the MPT by NMR in a non-enriched Ni–Ti sample

A quantitative evaluation of the volume fraction of the different phases present in thermoelastic equilibrium at each temperature can be obtained through spectral deconvolution after having subtracted the contribution of the broad satellite background. The area under each component constituting the NMR spectrum is proportional to the number of nuclei present in the corresponding phase. The volume fraction of a given phase can therefore be determined by calculating the ratio between the spectral area of that phase and the total spectral area. The NMR lines being of gaussian shape (or for the martensitic one can be approached by a sum of two gaussians), the evaluation of their spectral area can be simplified by determining the product (amplitude × full width at half height) of each contribution.

However, it is very difficult to follow the evolution of the MPT in the non-enriched Ni–Ti wires because the \(^{61}\)Ni NMR spectra have to be recorded at \( B_0 = 14 \) T where the austenitic line and the high frequency component of the martensitic line are superimposed at \( T < M_s \). To separate these two contributions it is necessary to know the relative amplitudes of the martensitic doublet. These relative amplitudes are characteristic of the distribution of grain orientation in a sample and are therefore temperature independent. Measurements of the relative amplitudes of the two martensitic components have thus been performed at very low temperature (130 K below \( M_s \)), where it can be assumed that no austenite is present in the sample any more.

In order to reduce the number of degrees of freedom to perform the deconvolution of the spectra obtained during the transformation (see Figs. 5(b) and (c)), the relative amplitudes of the martensitic doublet have been kept constant. The linewidth and the resonance frequency of the austenitic line, of the R-phase and of the two martensitic lines have been fixed at temperature-dependent values determined by extrapolating the temperature dependence observed above \( R_t \), between \( R_t \) and \( M_s \) and below \( M_t \) respectively. The obtained results are summarized in Table 2.

Before discussing them, it is important to remind that the
transformation temperatures of the wires reported in Table 1 were determined by the tangent method. The real transformation temperatures should be defined in a more correct way by the temperatures at which the DSC curve goes away from the baseline and joins it again. The \( R_s \) and \( M_f \) temperatures can thus be reappraised to \( R_{s,2} = 297 \) K and \( M_{f,2} = 213 \) K. However \( R_s \) and \( M_f \) cannot be determined by this second method since the two peaks are superimposed.

The number of measurements is not sufficient to describe in details the nucleation and growth process of the different phases, nevertheless, these results provide some interesting information. The \( A \rightarrow R \) phase transformation starts according to the DSC measurements between \( T = 297 \) K and \( T = 290 \) K. At a temperature \( T = 288 \) K, 62\% of the sample have already been transformed into R-phase. Then the transformation goes on at slower rate and at \( T = 275 \) K, 17\% of austenite are still detected.

The NMR measurements clearly shows that at \( T = 268 \) K, a non-negligible fraction of the sample (34\%) have already transformed into martensite, while this temperature is 5 K higher than the \( M_f \) temperature as determined by the tangent method. This result confirms that the DSC cannot give access to the real transformation temperatures of a sample when different peaks are superimposed.

At \( T = 238 \) K where the \( A \rightarrow R \) phase transformation should be completely finished, 6\% of austenite are still detected in the sample by the NMR measurements. It seems therefore that the whole sample does not undergo a \( A \rightarrow R \) phase transformation, or in other words that some regions of the sample transform directly from austenite into martensite.

At \( T = 204 \) K (9 K below \( M_{f,2} \)) 4\% of austenite are still present in the sample but there is no remaining R-phase. This fraction of austenite transforms then very slowly into martensite but the quantity involved is so small and the transformation rate so low that it cannot be detected by calorimetry. At \( T = 146 \) K, 98\% of the sample has transformed into martensite. The absence of austenite at \( T = 86 \) K was assumed to determine the relative amplitude of the two components of the martensitic line and perform the spectral deconvolution. It is therefore possible that some austenite is still present in the sample at this temperature and as a consequence that the fractions of retained austenite obtained at higher temperature are even larger. In any case, the NMR results clearly show that, in the Ni–Ti wires as in the \(^{61}\)Ni enriched bulk alloy, the MPT is not complete at a temperature well below \( M_f \) as determined by calorimetry.

### 3.2 Ni–Ti thin films

Figure 6 shows the \(^{61}\)Ni NMR absorption spectra at three different temperatures: (a) above \( R_s \), (b) between \( R_s \) and \( M_f \), and (c) below \( M_f \). It can be seen in Fig. 6(b) that the spectrum obtained at \( T = 248 \) K (18 K below \( R_s \)) is symmetric and presents no shoulder at the frequency corresponding to that of the austenitic line. This clearly shows that the whole sample has transformed into R-phase at this temperature.

Contrary to what was observed in the \(^{61}\)Ni enriched samples and in the Ni–Ti wires, there is no retained austenite at a temperature below \( M_f \) in the thin films sample, since the \( A \rightarrow R \) phase transformation is complete before the beginning of the R phase \( \rightarrow M \) transformation. However, it cannot be concluded immediately that these features are characteristic of thin films, the transformation sequences being different in the three kinds of sample. As a matter of fact, in the \(^{61}\)Ni enriched bulk alloy the transformation takes place directly from the austenite into the martensite and the \( R \)-phase transformation does not occur. In the Ni–Ti wires, the \( R \)-phase \( \rightarrow M \) transformation starts before the end of the \( A \rightarrow R \) phase transformation and the transformation takes place in two well-separated steps in the thin films.

In the \(^{61}\)Ni enriched Ni–Ti alloy and in the wires, where the \( R \)-phase transformation does not occur or is only partial, some small regions of the sample which are still in the austenitic phase may be “trapped” between martensite plates. The sample has then to be undercooled several degrees before these regions can transform into martensite. The transformation strain associated with the \( R \)-phase transformation being ten times lower than that of the martensitic transformation,\(^{9-11}\) this former transformation can proceed more easily than the latter one. It is therefore much less probable that the \( A \rightarrow R \) phase transformation may be hinder by the surrounding \( R \)-phase plates. As a consequence, when the transformation takes place in two-well separated steps, the whole sample can transform from austenite into R-phase.

It is well known that the presence of defects such as pre-
cipitates or dislocations supresses the martensitic transformation.\cite{10,11} This behaviour is explained by the formation of stress fields around them against the transformation. This effect cannot appear in our samples because the composition and heat-treatment of the wires and of the thin films have been chosen in such a way that the formation of precipitates is suppressed. It has been shown\cite{8} that the presence of precipitates can be clearly detected in the NMR spectra, particularly at $T > T_a$, where the signal of the additional phase is superimposed on the austenitic line. However a similar phenomenon could be responsible for the observations made in this work, the martensite plates playing the role of the “defects”.

When the R-phase transformation occurs the following martensitic transformation strain can be reduced by the amount of the R-phase transformation, that is nearly 10%. Moreover Ishida et al.\cite{11} have reported that twin deformation in some R-phase products might accommodate the local stress concentration introduced by the martensitic transformation when both transformations occur. These two phenomena may explain why there is no remaining R-phase at $M_f$ in the Ni–Ti wires.

It seems therefore that the occurrence of a well-separated A $\rightarrow$ R-phase transformation makes the MPT easier, allowing the whole sample to transform first into R-phase, and then into martensite, each step requiring less energy than the single A $\rightarrow$ M transformation. However complementary measurements in bulk alloys undergoing a two-distinct steps transformation would be necessary to determine if the difference in the growth process observed between the two kinds of sample has to be attributed to a difference in the transformation sequence or to a size effect.

4. Conclusions

In spite of the weak NMR sensitivity of $^{61}$Ni and the difficulties encountered to perform the deconvolution of the spectra recorded at $B_0 = 14 \, \text{T}$ in the presence of martensite and austenite, we have demonstrated that NMR is a very suitable tool to follow the evolution of the MPT in Ni–Ti SMA. This technique allowed us to obtain very interesting and quantitative information about the growth process of the different phases. The NMR results showed that in both bulk specimens, \textit{i.e.} the Ni–Ti wires and the $^{61}$Ni enriched Ni–Ti alloy, where the R-phase transformation does not take place or is only partial, the martensitic transformation is not complete even at temperatures well below $M_f$ as determined by calorimetry. On the other hand, in thin films showing a well distinct two-step transformation via the R-phase no remaining austenite could be detected below the $R_f$ temperature.

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REFERENCES


Appendix: NMR Basic Concepts

Nuclei of angular momentum $\vec{J} = (h/2\pi) \vec{T}$ and magnetic moment $\vec{m} = \gamma \vec{J}$ (where $\gamma$ is the gyromagnetic ratio) interact with a magnetic field $\vec{B}_0$ (Zeeman interaction) according to the Hamiltonian:

$$\mathcal{H} = -\gamma \frac{h}{2\pi} (\vec{T} \cdot \vec{B}_0) \quad (A.1)$$

Irradiating the sample by radiofrequency (rf) electromagnetic waves at the frequency $\nu_L = \Delta E / h = \gamma B_0 / 2\pi$, called the Larmor frequency, absorption of energy by the spin system is induced, and the NMR absorption spectra can be recorded. In absence of perturbation one line is observed at the frequency $\nu_L$.

Every nucleus experiences not only the applied static magnetic field but also a local magnetic field produced by its environment. For example, in metals and alloys, conduction electrons create at the nuclear position an average static magnetic field. This field shifts the NMR frequency $\nu_L$. The displacement of the resonance frequency is called the “Knight shift” and is defined as:\cite{12}

$$\mathcal{K} = \frac{\nu_m - \nu_L}{\nu_L} \quad (A.2)$$

where $\nu_m$ and $\nu_L$ are the resonance frequencies of the nucleus in the metallic material and in a non-metallic compound, respectively. When a metal undergoes a phase transition, $\mathcal{K}$ usually changes suddenly due to the change in local hyperfine interactions.

Another important parameter of a NMR spectrum is the width of the line. The basic contribution to the linewidth arises from the dipolar interaction between the nuclear spins. An additional inhomogeneous broadening of the line can be an indication of different effects, for example, magnetic inho-
mogeneities or Knight shift distribution due to the coexistence of phases with different shifts. The full width at half height (fwhm) of the NMR line is therefore correlated to the local atomic environment of the observed nuclei and constitutes an important parameter in the investigation of the MPT by NMR.

For nuclei with spin $I > 1/2$, the interaction of the nuclear quadrupole momentum $Q$ with the electric field gradient (efg) can drastically modify the NMR spectrum when the local symmetry is lower than cubic. First order quadrupolar interactions are responsible for the appearance of satellites transitions of weaker intensity symmetrically on each side of the central line. For powder or polycrystalline sample second order quadrupole interactions produce an asymmetric splitting of the central line. The width of the central line between the two maxima is given by:

$$\Delta \nu = \frac{25v_Q^2}{144v_L} \left( I(I+1) - \frac{3}{4} \right)$$

where $v_Q$ is the nuclear quadrupolar frequency, $v_Q = \frac{3eQV_{ZZ}(1-\gamma_\infty)}{2(2I+1)}$. $V_{ZZ}$ is the greatest component of the efg tensor and $(1-\gamma_\infty)$ is the antishielding factor, which depends on the polarizability of the core electrons of the given atom.

The equation (A.3) shows that in the case of an inhomogeneous broadening of the central line due to second order quadrupolar interaction, the width of the central line is inversely proportional to $v_L$ and therefore to the external applied magnetic field $B_0$. 
