AIP Conference Proceedings

# Internal field nuclear magnetic resonance: A versatile tool to study the structural and magnetic properties of ferromagnetic materials

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# Internal Field Nuclear Magnetic Resonance: A Versatile Tool to Study the Structural and Magnetic Properties of Ferromagnetic Materials

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**Abstract.** [59]Co-Internal Field Nuclear Magnetic Resonance (IFNMR), [57]Fe-IFNMR measurements are carried for the different materials like bulk cobalt, carbon coated cobalt (Co@C), bulk iron, carbon coated iron nanoparticles (Fe@C). The comparison of obtained results for bulk cobalt and Co@C shows that the bulk cobalt exists in the both the phases i.e., *fcc* and *hcp* phases, while the other exist only in the *fcc* phase. Further, the comparison of the NMR results of bulk iron and Fe@C confirms the presence of the single domain particles in the Fe@C samples. Thus, we propose IFNMR as a powerful tool to identify the structural and magnetic properties of ferro/ferrimagnetic materials.

## INTRODUCTION

In recent years magnetic nanomaterials are extensively studied due to their potential application in various fields such as magnetic toners, xerography, contrast agents, drug delivery, hyperthermia and other uses[1]. Interestingly, most of the physical and chemical properties of these magnetic materials are size dependent. For example bulk iron behaves as ferromagnetic when its size is in μm, whereas it transforms into superparamagnetism when the crystallite size gets reduced to nanometer (< 10 nm). Moreover, spintronic materials exhibit exotic magnetic properties with different local structures. These magnetic properties can be visualized through various available techniques such as Vibrating Sample Magnetometry (VSM), Mössbauer spectroscopy etc., However these techniques have few limitations. The VSM provides the saturation magnetization ($M_S$), retentivity and coercivity measurements, however the details related to the magnetic phase composition cannot be determined using this technique. Mössbauer Spectroscopy is limited to study the substances that containing only iron as an important composition. One can overcome these limitations using Internal Field Nuclear Magnetic Resonance (IFNMR) as an alternate tool. The working principle of IFNMR spectroscopy is almost similar to the traditional NMR except for the absence of external magnetic field. The internal magnetic field (hyperfine field) is acts as a resonating field. The resonance condition in IFNMR is given by[2],

$$f = \frac{\gamma H_{if}}{2\pi} \tag{1},$$

where, γ is the gyromagnetic ratio of the given NMR active nuclei (Hz/T), $H_{if}$ is the hyperfine field experienced by the NMR active nuclei (T), *f* is the resonance frequency (MHz). There are only few IFNMR active nuclei such as [53]Cr, [55]Mn, [57]Fe, [59]Co, [61]Ni etc., with their resonance frequency from ~ 10 to 700 MHz. Depending on the NMR active nuclei under the study the spectrometers can be built or modified.

# EXPERIMENTAL

IFNMR spectrometer used in the present studies was assembled in the lab. The details of our spectrometer have been reported elsewhere[3]. NMR signals in the magnetic samples have been observed using the different pulse sequences depending on the material under study. For pure metallic particles, we have used spin echo sequence ($\pi/2$ - $\tau$- $\pi$) have been employed. We applied a $\pi/2$ pulse of width 1.0 μs and the delay ($\tau$) between the two pulses is 25 μs for all the measurements. The $\pi/2$ pulse is optimized for the highest NMR spin-echo amplitude. Signal is recorded by measuring the spin echo amplitude as a function of frequency. Different frequency steps are preferred depending on the material. For iron nuclei, the step sizes of 0.05 MHz and for the cobalt 0.5 MHz are used. The scanning frequency range is also exclusively depends on the materials. For pure metallic iron the frequency ranges from 40-50 MHz and for the metallic cobalt ranges from 200-230 MHz. The quality factor (Q) of the probe circuit is maintained constant over the entire scanned range of frequencies. We have XRD measurements as a complimentary technique for NMR measurements for the $^{59}$Co IFNMR. We have used bulk iron, carbon coated iron nanoparticles, and carbon coated cobalt powder procured from M/S sigma Aldrich and the bulk cobalt from the M/S Alfa Aesar.

# RESULTS AND DISCUSSION

## (a) $^{59}$Co-IFNMR

It is well known that cobalt exhibits polymorphism at room temperature (RT) viz., Hexagonal Cubic Phase (*hcp*) and face centred cube (*fcc*) and both the phases coexist. The *hcp* and *fcc* phases both are close packed structures but different in their stacking order. The stacking order for *fcc* and *hcp* are ABCABC…. and ABABAB…, respectively. From earlier report it is evident that a single exclusive phase is preferred when low temperature methods are applied, while the existence of both phases is probable when synthesis is done using high temperature methods. Víctor et al.[4] have stated that the stability of the cobalt phase largely depends on particle size, metal salt reduction atmosphere and temperature. Dmitry et al.[5] have proved that low activation energy for the formation of the stacking faults is responsible for the existence of both the phases in the same sample under high temperature crystallization techniques such as melting-crystallization and evaporation-condensation. Further, they also suggested that low temperature solution chemistry methods yields exclusively single phase of cobalt. Due to these reasons the phase formation of cobalt is still debatable. In order to verify the phase composition $^{59}$Co IFNMR can be used as an alternate tool for XRD measurements as XRD peaks for *fcc* and *hcp* overlap and quantification estimation of phase composition is rather inconclusive. $^{59}$Co IFNMR studies were reported in the early 60's by Gossard et al.[6] Later, Kawakami et al.[7] reported the *hcp* phase of the cobalt through IFNMR. Later year's single domain cobalt particles are also studied using the same technique.

Figure 1(a) shows the $^{59}$Co-IFNMR spectra for bulk cobalt and Co@C measured at 300 K. Our observations at 300 K are in good agreement with the earlier reports[6,7]. For bulk cobalt, the main peak ~ 213 MHz are assigned to the domain walls of *fcc* phase while those three intermediate peaks appear in between 213 – 220 MHz are assigned to stacking faults of the *fcc* phase for the case of bulk cobalt particles. The frequencies corresponding to *hcp* domain wall and stacking defects corresponding to the *hcp* phase resonate at higher value of ~ 220 MHz and ~ 225 MHz. For single domain particles the peaks corresponding to the stacking faults are generally not observed, instead two more additional peaks along with the *fcc* and *hcp* domain wall occur at ~ 217.5 and ~ 224 MHz is corresponding to the *fcc* and *hcp* single domain cobalt particles. These observations are in good agreement with the earlier reports[8].

Another important observation is that the lower value of the resonance frequency for *fcc* cobalt is well documented in the earlier reports[7]. According to those reports, the *fcc* phase of cobalt experiences slight lesser the internal field (21.3 T) compared to *hcp* phase of cobalt (21.8 T). According to the equation 1 one can expect the resonance frequency of *fcc* phase of cobalt (213 MHz at RT) occur at slightly lesser value compared to *hcp* phase (220 MHz).

Comparing the $^{59}$Co-IFNMR spectra of these two samples, one can clearly notice that the NMR peaks corresponding to the *hcp* phase is almost invisible which indicates the presence of lesser amount (traces) of the *hcp* composition in the Co@C samples. On the other hand bulk cobalt exhibits the presence of both the phases. The XRD measurements are also in good agreement with our NMR measurements indicating the robustness of the IFNMR for the structural analysis. Thus, $^{59}$Co- IFNMR studies can also be used as a complimentary tool for X-Ray Diffraction measurements.
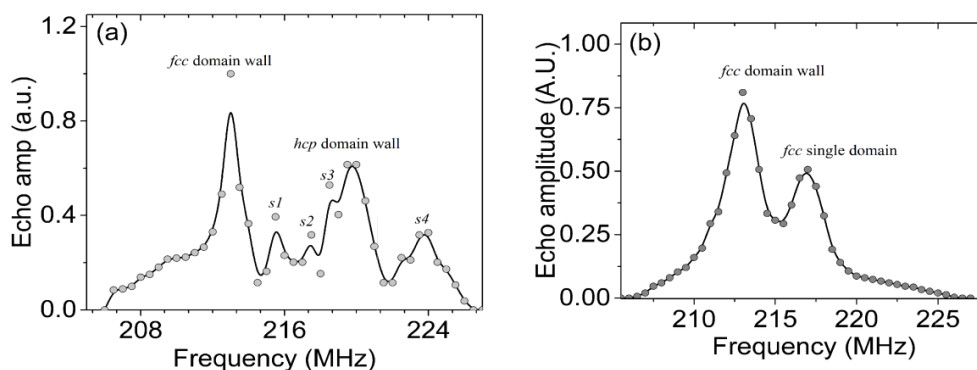
**FIGURE 1.**[59]Co-IFNMR spectra of (a) commercial cobalt sample (b) carbon coated cobalt nanoparticles measured at RT using a spin echo pulse sequence ($\pi/2$ - $\tau$- $\pi$).
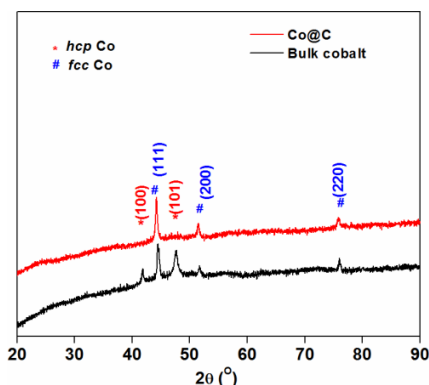


**FIGURE 2**.XRD measurements of (a) commercial cobalt sample (b) carbon coated cobalt nanoparticles.

# (b) Iron ($^{57}$Fe)

Internal field studies of iron was first studied and reported by Hanna et al.[9] using Mössbauer studies and it was estimated to be 33 T. IFNMR studies for bulk iron were estimated to be approximately 45.5 MHz at RT. Fig 2(a) and 2(b) shows the $^{57}$Fe NMR spectra for both bulk iron measured at RT and at 77 K. From the spectra one can clearly notice that the spectra extends for very narrow range of frequencies around $45.5 \pm 0.4$ MHz for RT, while, at $46.5 \pm 0.5$ MHz width for low temperature (77 K). The increase in the width of the signal for low temperature is ascribed to the raise of spontaneous magnetization and the increased NMR transition probability.

Further, we have performed $^{57}$Fe-IFNMR measurements for a single domain iron nanoparticles at room temperature, however, we have not observed any detectable signal at this temperature may be due to the thermal effects. At low temperature (77 K), we could able to observe a very weak signal which extends over ~ 1.5 MHz bandwidth around the centre frequency of ~ 46.6 MHz which is represented in the figure 2 (c). The observed NMR signal is deconvulated into two peaks using *Gaussian* fits. The fit curve indicates that there is an additional contribution to the NMR signal along with the domain walls of iron nanoparticles. This additional contribution is ascribed to the single domain iron particles. Thus, $^{57}$Fe-IFNMR can be used as a powerful tool to identify the domain state of magnetic materials.

Further $^{57}$Fe-IFNMR can be extended for the study of ferrimagnetic iron oxide, garnets and hexaferrite materials where the resonance frequencies lie between the ranges of 50-80 MHz.
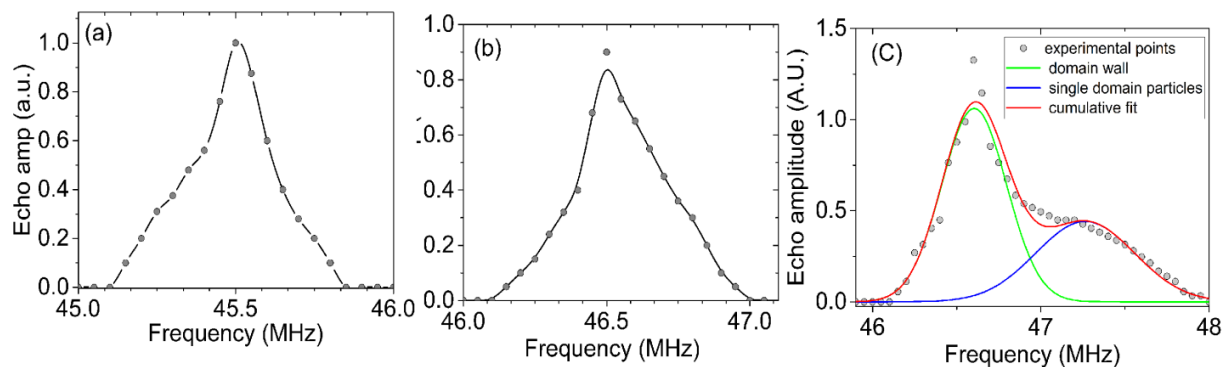
**FIGURE 3.** [57]Fe-IFNMR spectra of (a) commercial iron sample at RT (b) commercial sample at 77 K (c) carbon coated iron nanoparticles measured at 77 K. All the measurements are carried out using a spin echo pulse sequence ($\pi/2$ - $\tau$ - $\pi$).

## CONCLUSIONS

We have carried out [59]Co-IFNMR for bulk cobalt, Carbon encapsulated cobalt nanoparticles (Co@C) at RT. Obtained NMR results clearly confirms the presence of both *fcc* and *hcp* in bulk cobalt sample while, only the *fcc* phase in the Co@C. Further we have also performed [57]Fe-IFNMR measurements both at RT and at 77 K. [57]Fe IFNMR results confirms that bulk cobalt shows a narrow single peak, while the carbon coated iron nanoparticles (Fe@C) exhibits an extended peak with shoulder at ~ 47.2 MHz which is ascribed to the single domain iron nanoparticles. Thus the IFNMR technique can be used as a complementary tool to identify the structural and magnetic properties of pure ferro/ferrimagnetic particles.

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