Chapter 7

Magnetic Resonance study of
$\text{CoFe}_2\text{O}_4$/PVA matrix assisted film
ABSTRACT

In the previous chapters, we have studied the induced size effect on structural, magnetic and microwave resonance properties of CoFe$_2$O$_4$ nanoparticles, flow properties of particle size dependent ferrofluids and magnetic resonance properties of Co-Ferrite ferrofluid. **This present chapter expresses the effect on microwave resonance (absorption of microwaves) properties of orientation of magnetic spins in Co-ferrite NPs-PVA film and effect of radiation absorption on intensity of EPR spectra.**
7.1 Introduction

Nanomagnetic films are used in computer technology like magnetic storage. In magnetic thin films, the magnetization is uniform with respect to the thickness and is oriented in its plane. Such films, which are prepared in a magnetic field, have substantial magnetic anisotropy; the direction of easy magnetization is along the magnetic field. The important property of the magnetic thin films used in computer technology is the speed of their magnetization reversal when pulsed by a magnetic field. The orientation of magnetic spins plays a very important role in the magnetization reversal phenomenon in storage devices. Memory and logic devices based on the direction of rotation of the magnetization of the film elements are produced using magnetic thin films. The magnetocrystalline anisotropy should be very high for the magnetic films (it does not affected by external parameters like temperature) (Izv. AN SSSR: Seriafizika, 1972, vol. 36, no. 7). The CoFe$_2$O$_4$ NPs have very large magnetocrystalline anisotropy of the order of (with anisotropy constant $(K) = 2.2\text{ - }3.8 \times 10^6$ erg/cc). EPR is a big tool to study the magnetic structure of the thin film.

In this regard, we have made a very systematic study of CoFe$_2$O$_4$/PVA film by using EPR spectrometer. Temperature dependent properties like resonance field and peak-to-peak linewidth were also determined by EPR spectra in the temperature range of 4K-300K.

7.2 Experimental

7.2.1 Materials and synthesis of CoFe$_2$O$_4$ NPs-PVA Film
First, we have made CoFe$_2$O$_4$ nanoparticles by Massart’s method (see chapter 5). These NPs were then uniformly dissolved in PVA (Poly Vinyl Alcohol). PVA film was first heated to make it in gel form and then NPs were added into it. A magnetic stirrer was used to mix NPs uniformly into the PVA gel. A small drop of this solution was put on a rectangular glass plate and simultaneously a 1000G magnetic field was applied to give unidirectional order to the magnetic spins of NPs. This process remain for 2 days to dry the gel in the presence of white light using lamp by covering whole system by a glass jar to avoid contaminations from air. A schematic diagram was shown in Fig. 6.1.

Fig. 7.1 Schematic diagram of CoFe$_2$O$_4$/PVA thin film preparation process.

7.3 Characterization

Magnetic resonance (MR) measurements were performed using a Bruker EMX-10 EPR spectrometer using 100 kHz field modulation, an operating microwave frequency of about 9.85 GHz (X-band), and a TM011 mode cavity on magnetic film.
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7.4 Result and discussions

7.4.1 Ferromagnetic Resonance

7.4.1 (A) Angular dependent EPR Spectra at 300 K:

Angular dependent magnetic resonance spectra of as synthesized film were recorded to investigate the magnetic anisotropy in the plane of film. FMR is an experimental tool for measuring anisotropy energies, which has been applied with great success in the past, in particular to magnetic nanoparticles. A classical ferromagnetic approach using Landau-Lifshitz- Gilbert equation incorporated with thermal parameters is widely used to understand dynamics of fluctuating moments in these systems [1–4]. An alternative method to the above approach is proposed by Noginova et al. [5] where iron oxide MNPs were considered as a giant macrospin under quantization model to describe spectral linewidth, resonance condition and signal intensity.

The EPR spectra of film from angular rotation with angle ($\theta$) vary from 0-105° were shown in Fig. 7.3. Where $\theta$ is the angle between applied magnetic field and direction of magnetic film shown in Fig. 7.2

![Fig. 7.2 Schematic diagram of CoFe$_2$O$_4$/PVA film and applied magnetic field.](image)
The EPR spectra of film from angular rotation with angle (θ) vary from 95-195° and from 270-360° were shown in Fig. 7.4 and 7.5. The broad EPR spectra at room temperature showed the cluster-glass state with a peak to peak linewidth of 2000 Oe. First the orientation of magnetic film was confirmed by the variation of resonance intensity. When field was applied in the aligned direction of magnetic film, maximum intensity was observed which confirm the in-plane magnetic film.

Fig. 7.3 Schematic diagram of CoFe$_2$O$_4$/PVA film and applied magnetic field.

Further it was observed from the angular spectra that the resonance field ($H_r$) increases from 0° to 90° and again decreases from 90° to 180°.
Fig. 7.4 Schematic diagram of CoFe$_2$O$_4$/PVA film and applied magnetic field.

Fig. 7.5 Schematic diagram of CoFe$_2$O$_4$/PVA film and applied magnetic field.
The variation of resonance field with angular rotation was shown in Fig. 7.6. The observed angular variation of the resonance field, like for ferromagnetic resonance in thin films, is described by the well-known expression, which in addition to the electron Zeeman term also contains the demagnetization term with $ND = 4\pi$ [6]:

\[
\left( \frac{\omega}{\gamma} \right)^2 = [H_r - 4\pi M \cos 2\theta][H_r - 4\pi M \cos^2 \theta] \tag{1}
\]

Where $H_r$ is the resonance field at the microwave frequency $\omega$, $\gamma = 2\pi g \beta/h$ is the gyromagnetic ratio, and $M$ is the magnetization induced by the external magnetic field. In eq\(^\text{6}\) (1), $\theta$ is the angle between applied magnetic field and normal to the
plane of magnetic film but in our results $\theta$ is the angle between applied magnetic field and in the plane of magnetic film. So the results behaved like $\sin\theta$ not $\cos\theta$.

One can see from Fig. 7.6 that Eq. (1) describes the angular dependence of the resonance field quite well. Note that the magnetization can be directly measured by the difference between actual resonance field $H_{r0}$ and the field defined by solely the $g$ factor, i.e., measured at high temperatures, where $M \to 0$.

$$4\pi M = H_r - h\nu/g\beta \quad (2)$$

The observations also could be explained in terms magnetic anisotropy [7]. The magnetic anisotropy of the film in the plane of magnetic film was less compared to the other angular rotation and have maximum value at $\theta = 90^\circ$. This was also confirmed the eq\(^n\) (1).

**7.4.1 (B) Angular variation of EPR Linewidth:**

The EPR linewidth shows the sine wave [8] like nature with angular rotation.

Fig. 7.7 Angular dependence of peak-to-peak linewidth measured in the plane of the film at 300 K showing $180^\circ$ periodicity.
shown in Fig. 7.7. When θ=0°, the peak-to-peak linewidth was observed to be less and subsequently increases with increasing angle up to θ=90°. It may be due to increasing anisotropy and exchange interactions [9]. There was no change in resonance field (Hr) and peak-to-peak linewidth when EPR spectra taken in a perpendicular direction of film. Spectra from 0-360° were shown in Fig. 7.8. 

![Magnetic resonance spectra of Film in the plane normal to the plane of magnetic film at 300 K.](image)

Further it was also observed that film did not come into its original state from 0-360° angular rotation (see Fig. 7.9). This type of materials can be used for microwave absorbing material [10].
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7.4.1 (C) Temperature dependent EPR spectra:

Temperature dependent EPR spectra in the temperature range of 20-130 K were shown in Fig. 7.10. The spectra shifts towards higher field i.e. resonance field was increasing upto 130 K and then decreasing shown in Fig. 7.10. It may be due to increasing anisotropy at low temperatures [12] and may be due to spin-glass to cluster-glass transition. It may be the blocking temperature ($T_B$) for the
CoFe$_2$O$_4$ nanoparticles from where resonance field (Hr) starts decreasing; it was 132 K from the Fig. 7.11.

![Graph showing temperature dependence of resonance field](image)

Fig. 7.11 Temperature dependence of the resonance field measured in the plane of the film.

### 7.5 Conclusion

Matrix assisted film of CoFe$_2$O$_4$/PVA was successfully prepared to probe its magnetic resonance parameters. We reached in successful results. The Resonance field shows sin$\theta$ dependence and Peak-peak linewidth shows also sin$\theta$ dependence. The results can be used to probe the magnetocrystalline anisotropy and can be used in such type of devices. The film did not come at its equilibrium state after a complete angular cycle. This type of materials can be used in microwave absorbing devices.
References


