

## **Characterization of different magnetite–cobalt nanoparticles in hydrocarbon-based magnetic fluids by means of static and dynamic magnetization measurements**

Oscar Ayala-Valenzuela, Paul C. Fannin, Rebeca Betancourt-Galindo, Oliverio Rodríguez-Fernández, José Matutes-Aquino

### **Abstract**

Magnetic nanoparticles with different compositions ( $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ ,  $0 < x < 0.1$ ) were synthesized from metal salts using a coprecipitation technique to produce magnetic fluids following a peptization technique. The liquid carrier was the hydrocarbon Isopar M and the surfactant was oleic acid. The colloidal-sized ferrimagnetic nanoparticles produced were found to be superparamagnetic. Measurements of the complex magnetic susceptibility were carried out to evaluate the resonant frequency  $f_{\text{res}}$ , the anisotropy constant  $K$ , and anisotropy field  $H_A$ .  $f_{\text{res}}$  was found to be a linear function of the cobalt content of the magnetic nanoparticles over the range of cobalt content studied.

### **Introduction**

Magnetic nanoparticles exhibit interesting magnetic properties that can be very different from those of the bulk material. Specifically, if the particles are sufficiently small, ferromagnetic and ferrimagnetic materials will become superparamagnetic, that is, above a certain temperature known as the blocking temperature, their magnetization curves show no hysteresis. In fact, all relevant magnetic properties (coercivity, blocking temperature, saturation magnetization, and remanent magnetization) are functions of particle size, shape and surface chemistry [1,2]. It is a well-known fact that the chemical

coprecipitation method is an economical way of producing ultrafine particles [3].

Magnetic fluids are ultrastable colloidal suspensions of submicron sized, ferromagnetic or ferrimagnetic particles in liquid carriers such as hydrocarbons [4] and are used in rotating shaft seals, exclusion seals, loudspeakers, dampers, inclinometers, medical applications, etc. [5].

In this work, we briefly describe a method to produce magnetic fluids and also characterize the magnetic fluids synthesized. We obtained five different samples from the system with chemical composition  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$  ( $x = 0.0, 0.04, 0.06, 0.08$  and  $0.1$ ). Vibrating sample magnetometry (VSM) and the short-circuited transmission line technique were used to characterize the superparamagnetic properties of the nanoparticles in the synthesized fluids.

### **Experimental details**

$\text{Co}_x\text{Fe}_{3-x}\text{O}_4$  ( $x = 0.0, 0.04, 0.06, 0.08$  and  $0.1$ ) nanopowders were synthesized by a chemical coprecipitation technique [6] from JT Baker reagent grade chemicals, namely,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (Aldrich) and  $\text{NH}_4\text{OH}$ . Stoichiometric ratios (1:2) [ $\text{Fe}^{2+}, -\text{Co}^{2+}:\text{Fe}^{3+}$ ] at 0.1 M solutions were mixed and heated at  $70^\circ\text{C}$  with continuous stirring. A black precipitate was obtained after the rapid addition of  $\text{NH}_4\text{OH}$  at 10%. A peptization process at  $80^\circ\text{C}$  and a mechanical stirrer rotating at a speed of 1000 rpm were used to synthesize the magnetic fluids. For the five different magnetic fluids, the liquid carrier was Isopar M (Exxon Mobil Chemical) while the surfactant was oleic acid (JT Baker).

The magnetic properties of the nanoparticles and fluids were determined using a VSM LDJ Electronics model 9600 at room temperature.

Measurements of the complex magnetic susceptibility,  $X(\omega) = X'(\omega) - iX''(\omega)$ , over the frequency range from 100MHz to 6GHz were carried out by the short-circuited coaxial transmission line technique [7]. Measurements were made by means of an Agilent Vector Network Analyzer 8753ES and a 50 $\Omega$  coaxial line incorporating a coaxial cell. The coaxial cell containing the magnetic fluid sample was terminated in a standard short-circuit load, the real,  $X'(\omega)$ , and imaginary components,  $X''(\omega)$ , of the complex magnetic susceptibility were determined.

## Results and discussions

Fig. 1 shows the room temperature magnetization curves of the magnetic fluids with nanoparticles of formula  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$  ( $x = 0.0, 0.04, 0.06, 0.08$  and  $0.1$ ). All the curves show reversible magnetization due to the superparamagnetic behavior of the magnetic nanoparticles. The magnetization curves show high-field susceptibility (the samples do not saturate), which can be attributed to a superficial spin disorder when the nanoparticle surface has significant roughness and high broken bond density [8].

$f_{\text{res}}$  is the ferromagnetic resonance frequency defined as the frequency when the  $X'(\omega)$  component goes from a positive to a negative quantity, as indicated by the solid lines in Fig. 2 [7] while  $f_{\text{max}}$  is defined as the frequency corresponding to the maximum of the  $X''(\omega)$  component, as indicated by the dash-dot lines in Fig. 2. Fig. 2 also shows that both  $f_{\text{res}}$  and  $f_{\text{max}}$  increase to higher frequencies with increasing cobalt content. Apart from indicating the presence of resonance, the  $X''(\omega)$  and  $w'(\omega)$  components also show effects that are manifestations of the contribution of the relaxational Néel components to the susceptibility. The presence of a resonant behavior characterized by

the precession of the magnetic moment about the easy axis of magnetization in a particle was also revealed for each of the five samples.

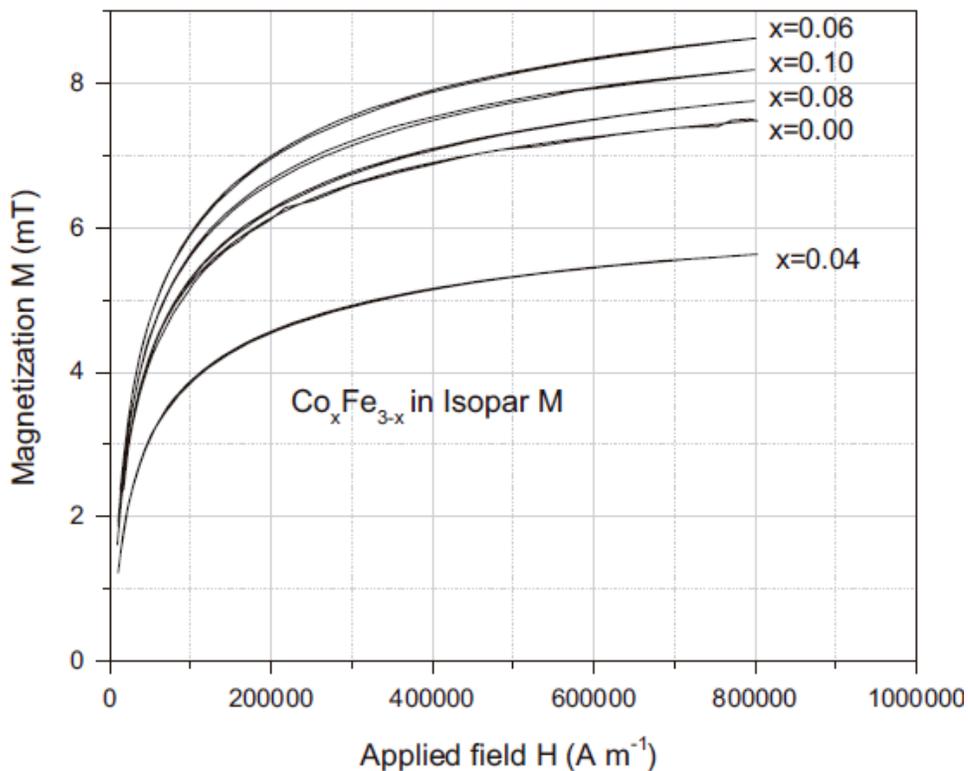


Fig. 1. Magnetization curves of the five magnetic fluids.

Considering the calculation made by Van Dyck et al. 1987 and Van Dyck 1990 [9,10] for the gyromagnetic ratio of free electron  $\gamma = 2.002 \times 10^5 \text{ mA}^{-1} \text{ s}^{-1}$ , the anisotropy field,  $H_A$ , can be calculated from the angular resonant frequency given by  $\omega_0 = \gamma H_A$ . The anisotropy field is given by  $H_A = 2K/M_S$ , where  $K$  is the anisotropy constant and  $M_S$  is the saturation magnetization per unit volume [7]; a value of  $M_S = 0.4 \text{ T}$  was assumed for all samples. Values of  $H_A$ ,  $K$ , and  $f_{\text{res}}$  obtained for the five fluids are shown in Table 1; a value of  $g = 2.002 \times 10^5 \text{ mA}^{-1} \text{ s}^{-1}$  was used in each case. From Table 1, it is seen that with

increasing cobalt content, there is a systematic increase in  $K$  and  $H_A$ , this increase is associated with the magnetic anisotropy introduced by the cobalt ion.

Fig. 3 shows the plot of  $f_{res}$  data against the cobalt content of the samples together with an associated linear fit. This linear fit indicates that one can predict the behavior of  $f_{res}$  by controlling the cobalt content of the samples. Also, if a linear behavior is valid for higher values of cobalt content then the possibility of tailoring magnetic fluids with specific values of  $f_{res}$  over the approximately range 2.64–32GHz becomes a real possibility.

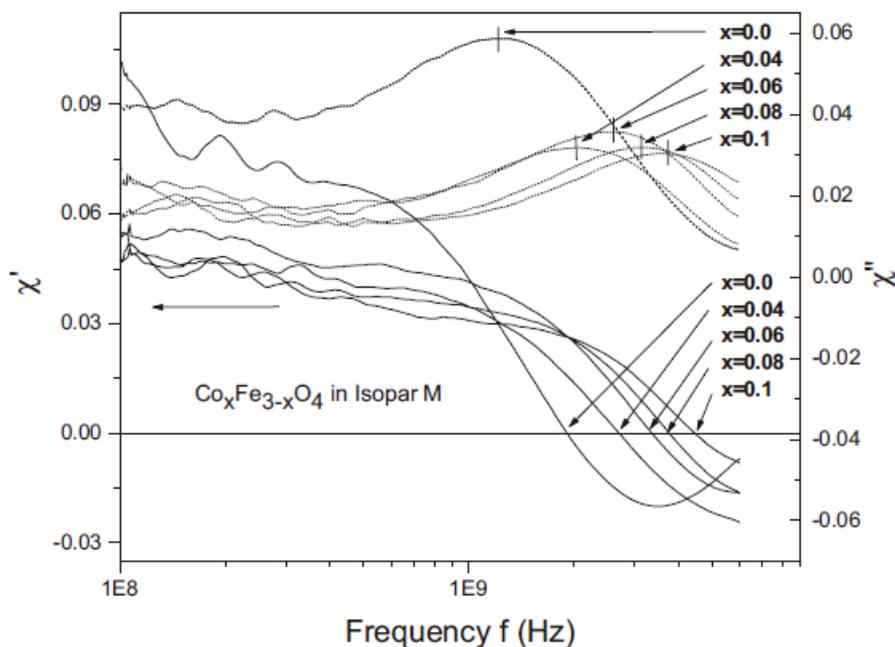


Fig. 2. Plot of  $\chi'(\omega)$  and  $\chi''(\omega)$  against  $f(\text{Hz})$  for the five magnetic fluids.

Table 1  
Fluid parameters

	$M_S$ (mT)	$H_A$ (kA m <sup>-1</sup> )	$K$ (kJ m <sup>-3</sup> )	$f_{res}$ (GHz)
Fe <sub>3</sub> O <sub>4</sub>	7.5	60.3	12.06	1.92
Co <sub>0.04</sub> Fe <sub>2.96</sub> O <sub>4</sub>	5.6	82.9	16.58	2.64
Co <sub>0.06</sub> Fe <sub>2.94</sub> O <sub>4</sub>	8.6	106.2	21.24	3.38
Co <sub>0.08</sub> Fe <sub>2.92</sub> O <sub>4</sub>	7.7	120.0	24.0	3.82
Co <sub>0.1</sub> Fe <sub>2.9</sub> O <sub>4</sub>	8.2	141.3	28.26	4.5

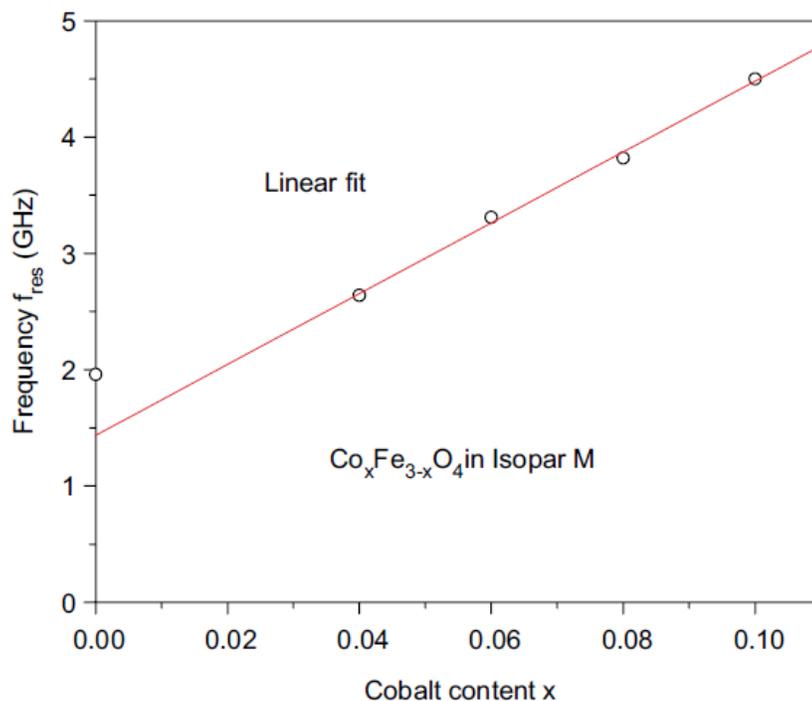


Fig. 3. Plot of the dependence of the resonant frequency  $f_{res}$ , as a function of the cobalt content of the magnetic nanoparticles of the different magnetic fluids investigated.

## Conclusions

Magnetization curves of the five magnetic fluids presented, show high-field susceptibility (the samples did not saturate) and a superparamagnetic behavior of the obtained magnetic materials was also found.

A systematic increase in the anisotropy constant,  $K$ , and of the corresponding anisotropy field,  $H_A$ , was observed when the cobalt content was increased; this effect is associated with the magnetic anisotropy introduced by the cobalt ion.

By means of complex susceptibility measurements, the presence of resonance was found in all five samples; the resonant frequency ( $f_{res}$ ) range being 1.92–4.5 GHz. Also from linear fits of the plot of  $f_{res}$  against the cobalt content of the samples it has been indicated that one can predict the behavior of  $f_{res}$  by controlling the cobalt content

of the samples. This fact has interesting practical implications and is currently the topic of further investigations.

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