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SPIN RESONANCE INVESTIGATIONS ON WATER-BASED MAGNETITE FERROFLUID

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In this work, we have investigated a water-based ferrofluid for its magnetic properties. The nanoparticles of ferrofluid were synthesized by a chemical coprecipitation route. Magnetite nanoparticles were chemically prepared by coprecipitation of reverse micelles in the aqueous phase. A very low observed value of saturation magnetization, i.e. 1 emu/g, and the magnetic anisotropy energy constant were found in the samples. This was explained by dead layer theory and effect of double surfactant coating. Ferromagnetic resonance (FMR) measurements were performed via zero-field-cooled (ZFC) protocol. The Neel–Brown model was applied by assuming the resonance field as the applied field on the superparamagnetic system. Under these circumstances, the ratio of magnetic anisotropy energy to thermal energy was calculated and it is found that it becomes unity ~225 K for the particles, which are antiparallel to the applied field.

1. Introduction. The existence of blocking effects in nanomaterials is characterized by a critical temperature, i.e. a blocking temperature (T_b). In addition to its temperature dependence, T_b also depends on other key factors like the volume of particles (V), magnetic anisotropy (K) and the timescale of the measuring instrument (τ_m), making it as one of the ill-defined parameters in nanomagnetism [1]. When the timescale window is large than the superparamagnetic relaxation time (τ) then the system displays superparamagnetism. On the other hand, when $\tau > \tau_m$, the system is measured to be in the blocked state. In this state, the quasi-static properties of the system are observed. Many techniques have been employed to ascertain T_b in such systems and among them the most frequently used ones are Superconducting Quantum Interference Device (SQUID), Vibrating Scanning Magnetometer (VSM), ac-susceptibility measurements and Mossbauer spectroscopy [1, 2]. But the ability of FerroMagnetic Resonance (FMR) for finding T_b has been explored only in a few cases [3, 4]. The aim of this work is to study the dynamic phase transition from ferromagnetic to superparamagnetic state in a water-based magnetite ferrofluid by using the famous Neel–Brown model in FMR results.

2. Synthesis and experimental methods. Fe_3O_4 nanoparticles (FNPs) were synthesized via a chemical route. A detailed schematic diagram of the synthesis procedure is shown in Fig. 1. The structural characterization was performed using a powder X-ray diffractometer and HRTEM. The magnetization measurements were made on these samples by a Lakeshore make VSM model 7400. The ferromagnetic resonance (FMR) measurements were made using an M/s Bruker biospin model A300. Before measurements, the signal channel was calibrated at room temperature using the 1 mg DPPH standard.

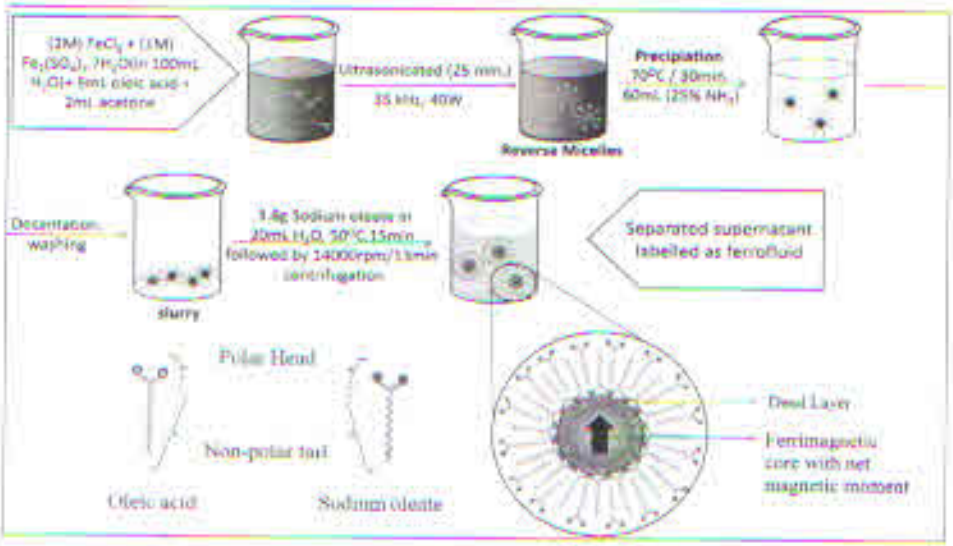

Fig. 1. Schematic diagram of synthesis of MNPs.

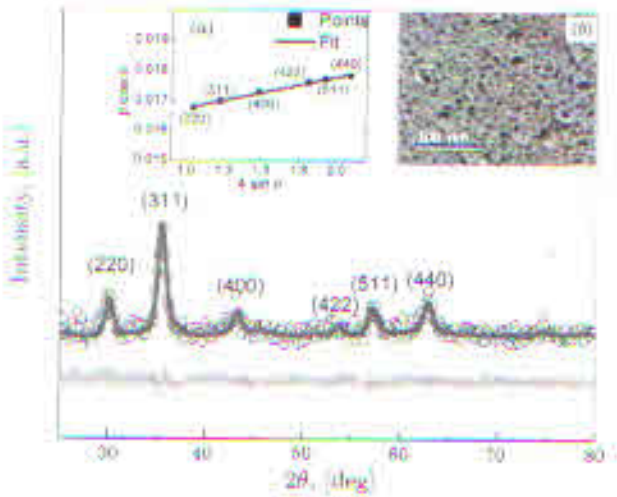

Fig. 2. Room temperature X-ray diffraction pattern of Fe_3O_4 nanoparticles with rietveld refinement. The inset shows (*a*) the micrograph from transmission electron microscope (TEM), (*b*) a Williamson–Hall plot.

3. Results and discussion.

3.1. Structural characterization. Fig. 2 shows the Powder X-ray Diffraction Pattern (PXRD) pattern of Fe_3O_4 ferrofluid drops dried on a glass slide in ambient conditions. The refined peak positions (2θ) and the full width at half-maximum (FWHM) values (β) obtained from rietveld refinement were used in the Williamson–Hall equation $\beta\cos\theta = 4\varepsilon\sin\theta - \lambda/D$ to calculate the average crystallite size (D) and the strain (ε) induced in the NPs, where λ is the wavelength of X-ray (inset (*a*)). The average crystallite size (D) and the strain (ε) were found to be 9.8(1) nm and 0.0010(1), respectively. The inset (*b*) shows the morphological view of the NPs. The average particle size was calculated by counting over 150 NPs and found to be 10.9 nm with the standard deviation $\sigma = 2.8$ nm.

3.2. Magnetic measurement. The magnetization loop of such Fe_3O_4 ferrofluid was recorded at room temperature, as shown in Fig. 3. The loop shows a

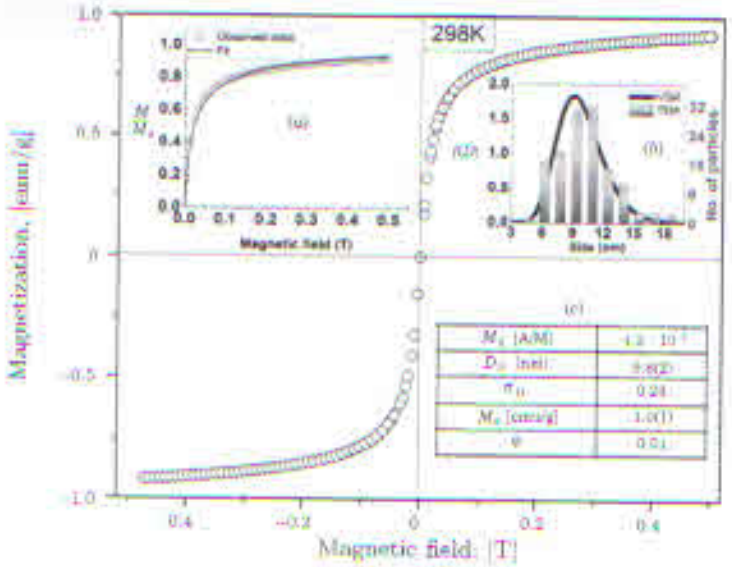

Fig. 3. Hysteresis loop of the Fe_3O_4 ferrofluid at room temperature. Inset (*a*): magnetization curve with fit; inset (*b*): particle size distribution from VSM and TEM results.

negligible hysteresis with 2.5 Oe as the coercive field (H_c) value, which evidences that the particles are of superparamagnetic nature. The magnetic state of such a system can be described by [5, 6]

$$M = \int_0^\infty L(D) f(D) \mathrm{d}D, \tag{1}$$

where

$$L(\alpha) = M_s^f \left(\mathrm{cth}\alpha - \frac{1}{\alpha} \right), \quad \alpha = \frac{\mu H}{kT}, \quad M_s^f = M_d \varphi ;$$

$$f(D) = \frac{1}{\sqrt{2\pi}\sigma_D D} \exp\left\{ \frac{-\ln(D/D_0)^2}{2\sigma_D^2} \right\}, \quad \int_0^\infty f(D)\mathrm{d}D = 1.$$

Here $L(\alpha)$ is the Langevin function, $f(D)$ is the lognormal size distribution, μ is the magnetic moment, σ_D is a standard deviation, H is the applied magnetic field, k is the Boltzmann constant, T is the temperature, M_s^f is the fluid magnetization, φ is the volume fraction of FNPs in the ferrofluid (FF), M_d is the domain magnetization, and D_0 is the median diameter. Inset (*a*) shows the best fit to the M-H curve yielding the particle size distribution from VSM. It must be noted that the saturation magnetization M_s^f is very low, i.e. 1 emu/g if compared to the bulk value 84 emu/g.

3.3. FMR measurement. These measurements on the sample were made using the 9.54 GHz microwave frequency with a power of 1.03 mW. The sample was cooled down from 298 K in zero magnetic field to 4 K and the spectra were recorded while raising the temperature. During the field-cooled measurement, the sample was cooled in a magnetic field (H_{app}) of 1 T and the spectra were recorded at 4 K with 0° and 90° in plane angular orientations. By applying a linear model [9], the anisotropy in the sample was found to be 340 Oe at 4 K with $M_s = 1$ emu/g. So, the applied field is simply expected to align all moments in one direction thus

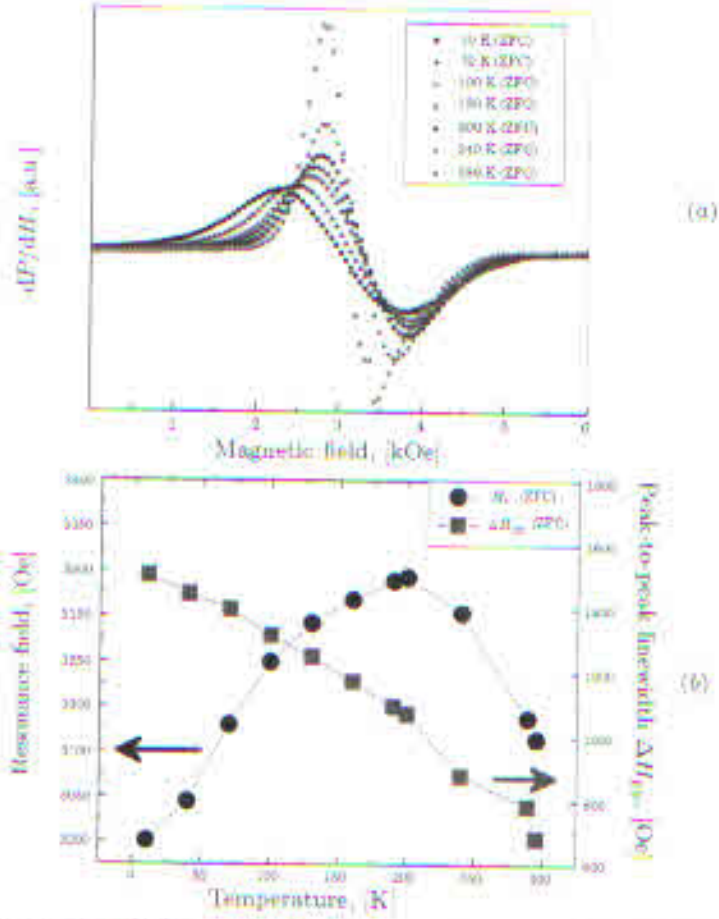

Fig. 4. — (a) Selected FMR spectra in the temperature range (4 – 298 K) with ZFC protocol. (b) Variation of the resonance field and line width with the temperature.

minimizing the orientational distribution function [10]. Fig. 4 shows the recorded low temperature FMR spectra.

In ZFC, the resonance field shows a non-monotonic behavior with a maximum of ~200 K. On the other hand, ΔH_{pp} shows a regular fall characteristic of the FNPs with an increase in temperature [11]. Such temperature dependence of line width in a system composed of magnetic nanoparticles will be described elsewhere in detail.

To explain the behavior of H_r, we employed the most frequently used Neel–Brown model. With the Neel–Brown model, the relaxation time between double potential wells for an ideal superparamagnetic system in the absence of any field is given by $\tau = \tau_0 \exp\{U/kT\}$; $U = KV$, where τ is the superparamagnetic relaxation time, τ_0 is the pre-exponential factor, U is the magnetic anisotropy energy, k is the Boltzmann constant, and T is the temperature. But to determine the magnetic phase of the system (i.e. ferromagnetism/superparamagnetism) and to ascertain the blocking temperature of the system, we need to apply some finite amount of magnetic field and then we directly measure the magnetic property of the system like magnetization or susceptibility. This situation results in the alignment of more magnetic moments parallel to the applied field (H) if compared to the antiparallel configuration. In other words, an ideal double potential describ-

ing a superparamagnetic system is now perturbed to a distorted double potential well system separated by the activation energy barrier, which will change from $E_a = KV$ to $E_a^- = KV(1 - H/H_a)^2$ and to $E_a^+ = KV(1 + H/H_a)^2$ for the antiparallel and parallel configurations, respectively. It is now clearly visible that the former with a lesser energy barrier will play an important role if compared to the latter one in determining the unblocked state. The extent of perturbation depends on the strength of the applied field H. In DC-magnetization and AC-susceptibility measurements, the system is placed in a magnetic field with the condition $H < H_a$. The blocking effects in such an environment are observed as soon as the available thermal energy becomes enough to flip the antiparallel moments to make them parallel along the field. The blocking temperature is observed when the superparamagnetic relaxation time matches with τ_m. Under these circumstances, the model under discussion gets modified mathematically and can be expressed as follows [12]:

$$\tau^{\pm} = \tau_0 \exp\left\{\frac{U}{kT}\right\}; \quad U = KV\left(1 \pm \frac{H}{H_a}\right)^2. \tag{2}$$

In addition to this, it is expected that Larmor relaxation processes in these classical spin system is affected by the superparamagnetic relaxation mechanism of MNPs. In this way, the resonance field (H_r) can be regarded as a manifestation of two competitive dynamic changes taking place in the system. Using requisite values ($M_s = 1$ emu/g, volume corresponding to $D = 9.8$ nm, $H_a = 340$ Oe, $H = H_r$, $K = 85\,\mathrm{Jm^{-3}}$, $k = 1.38 \cdot 10^{-23}\,\mathrm{JK^{-1}}$) in Eq. (2), we calculated U/kT for the parallel/antiparallel potential well of Fig. 5 corresponding to the ZFC resonance field values of FMR, and its variation with the temperature is shown in Fig. 6a. A close look of Fig. 6b shows that $U/kT = 1$ is found exactly near to a temperature region (~222 K), where the system loses nearly all its anisotropy in the angular dependent FC measurements (not shown). Our derived data in Fig. 6b resemble the Mossbauer results discussed by Rondinone *et al.* [2]. But simultaneously, the blue curve representing the relaxation from the potential well with parallel configuration is still not able to cross $U/kT = 1$, which is due to hindrance by a very high energy barrier created from the large magnitude of the applied field over the anisotropy field ($H = H_r \gg H_a$). As a result, due to the enhanced energy barrier resulting for FNPs in an aligned potential well makes the dynamic relaxation process infeasible from this well even above T_b. From Fig. 6b, we conclude that the observed temperature region ~225 K shows the blocking effects in the system.

4. Conclusion. A double surfactant water-based magnetite ferrofluid was chemically synthesized and studied for its structural and magnetic properties by

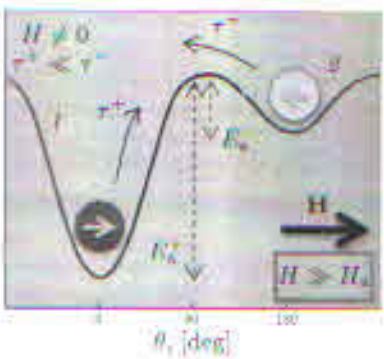

Fig. 5. A highly distorted double potential well system in FMR with $H_r = H \gg H_a$.

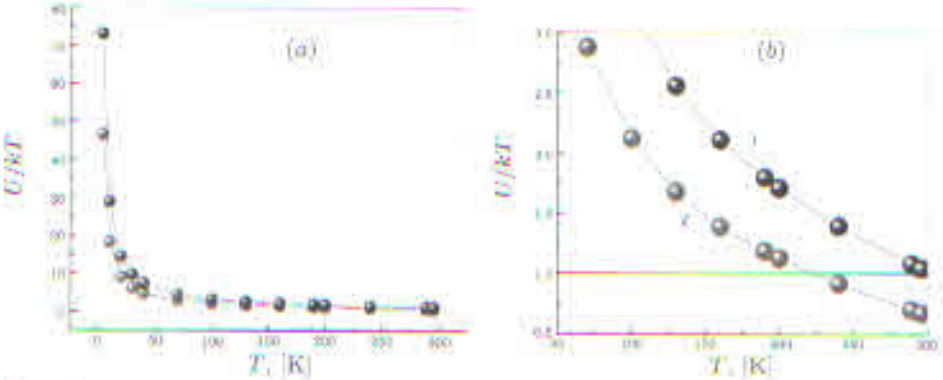

Fig. 6. (*a*) Variation of U/kT vs. T for ZFC dataset; (*b*) a magnified view of the region, where U/kT becomes unity

XRD, TEM, VSM and FMR techniques. The magnetic nanoparticles were found to be with a very low saturation magnetization (M_s). This was explained with the explanation of dead layer, double surfactant coating. The low temperature analysis of FMR data in the ZFC protocol revealed interesting features. The resonance field in ZFC shows maxima at ~200 K. The application of a linear model and a Neel–Brown model to the FMR shows the blocking effects in the system at ~225 K. These effects were attributed to the flipping caused by particles in the antiparallel potential well.

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REFERENCES

[1] M.A. Willard, L.K. Kurihara, E.E. Carpenter, S. Calvin, V.G. Harris. Chemically prepared magnetic nanoparticles. *International Materials Reviews*, vol. 49 (2004), pp. 3–4.

[2] A.J. Rondinone, C. Liu, Z.J. Zhang. Determination of magnetic anisotropy distribution and anisotropy constant of manganese spinel ferrite nanoparticles. *J. Phys. Chem. B*, vol. 105 (2001), pp. 7967–7971.

[3] R. Berger, J.C. Bissey, J. Kliava, H. Daubric, C. Estournès. Temperature dependence of superparamagnetic resonance of iron oxide nanoparticles. *J. Magn. Magn. Mater.*, vol. 234 (2001), pp. 535–544.

[4] K. Usadel. Temperature-dependent dynamical behavior of nanoparticles as probed by ferromagnetic resonance using Landau–Lifshitz–Gilbert dynamics in a classical spin model. *Phys. Rev. B*, vol. 73 (2006), pp. 212405.

[5] R.C. Woodward, J. Heeris, T.G. St Pierre. A comparison of methods for the measurement of the particle-size distribution of magnetic nanoparticles. *Appl. Cryst.*, vol. 40 (2007), pp. s495–s500.

[6] R.V. Upadhyay, K. Parekh, R.V. Mehta. Spin-glass transition in a model magnetic fluid: Electron spin resonance investigation of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles dispersed in kerosene. *Phys. Rev. B*, vol. 68 (2003), pp. 224434.7.

[7] T. Kim, M. Shima. Reduced magnetization in magnetic oxide nanoparticles. *Journal of Applied Physics*, vol. 101 (2007), pp. 09M516.

[8] C.J. OConnor, Y.S.L. Buisson, S. Li. Ferrite syathesis in microstructured media: Template effects and magnetic properties. *J. Appl. Phys.*, vol. 81 (1997), pp. 4741.

[9] J.M. Vargas, E. Lima, R.D. Zysler. J.G.S. Duque, E. Biasi, M. Knobel. Effective anisotropy field variation of magnetite nanoparticles with size reduction. *Eur. Phys. J. B*, vol. 64 (2008), pp. 211–218.

[10] N. Noginova, F. Chen, T. Weaver, E.P. Giannelis, A.B. Bourlinos, V.A. Atsarkin. Magnetic resonance in nanoparticles: between ferro- and paramagnetism. *Journal of Physics: Conden. Mat.*, vol. 19 (2007), pp. 246208.

[11] K.H. Hsu, J.H. Wu, Y.Y. Huang, L.Y. Wang, H.Y. Lee, J.G. Lin. Critical size effects on the magnetic resonance in Fe_3O_4 nanoparticles. *J. Appl. Phys.*, vol. 97 (2005), pp. 114322I–143224.

[12] R.K. Zheng, H. Gu, B. Xu, X.X. Zhang. The origin of the non-monotonic field dependence of the blocking temperature in magnetic nanoparticles. *J. Phys.: Conden. Mat.*, vol. 18 (2006), pp. 5905.

[13] D. Serantes, D. Baldomir. Superparamagnetism and Monte Carlo simulations. *Open Surf. Sci. J.*, vol. 4 (2011), pp. 71–84.

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