PRAMANA
— journal of
physics

© Printed in India

Vol. 45, No. 5,
November 1995
pp. 419–430

Temperature dependence electron spin resonance spectra of a magnetic fluid

R V UPADHYAY, D SRINIVAS[+], R V MEHTA and P M TRIVEDI
Department of Physics, Bhavnagar University, Bhavnagar 364002, India
[+] Central Salt and Marine Chemical Research Institute, Bhavnagar 364002, India

MS received 27 February 1995; revised 3 August 1995

Abstract. ESR spectra of a laboratory synthesized kerosene base magnetic fluid containing ultrafine magnetic particles (average diameter of 100 A) of $Zn_{0.1}Fe_{0.9}Fe_2O_4$ are recorded at different temperatures. A narrow signal was observed above the melting point of the carrier liquid (200 K) which can be attributed to a very small volume fraction of superparamagnetic particles in the system. The peak-to-peak line width for both low and high field cooled configurations show an increase with decreasing temperature. This observed behaviour has been explained by considering various energy terms which contribute to the line width.

Keywords. Magnetic fluid; ESR; temperature dependence.

PACS Nos 76·50; 75·50; 75·60; 75·30

1. Introduction

Sterically stabilized colloidal dispersions of ultra-fine single domain ferro- or ferrimagnetic particles resemble superparamagnetic materials at room temperature. These colloids called magnetic fluids or ferrofluids do not exhibit hysteresis behaviour or coercivity [1]. Under the action of externally applied gradient magnetic fields such a fluid can develop structural order similar to those in crystalline solids [2] or dipolar glasses [3] and hence it can serve as a model system to study characterization of condensed materials. Magnetic and Mössbauer measurements have been extensively used to study the superparamagnetic behavior of particles dispersed in liquid carriers [4–8]. It has been demonstrated that electron spin resonance (ESR) is a complimentary tool for the investigation of ultra-fine colloidally dispersed magnetic particles [8–11]. Usually, ESR spectra of magnetic fluids are recorded at room temperature and peak-to-peak linewidth (ΔH_{pp}) and the resonance field (H_r) are also reported for superparamagnetic particles dispersed in solidified kerosene [12]. A magnetic fluid exhibits both superparamagnetism at one temperature (above the melting point of the carrier liquid, T_m) and may exhibit magnetic anisotropy at lower temperatures depending upon the particle size [1]. Hence it will be of interest to investigate the temperature dependence of ΔH_{pp} from room temperature to well below the melting point of the carrier.

In this paper we report the results of our investigation of ESR spectra of a laboratory synthesized magnetic fluid, $Zn_{0.1}Fe_{0.9}Fe_2O_4$ for different temperatures.

2. Experimental

There are a number of preparation methods available for the synthesis of fine ferrite particles [13–17]. In the present case we have used the co-precipitation technique to prepare ultra-fine particles of $Zn_{0.1}Fe_{0.9}Fe_2O_4$. Analytical reagent grade $FeCl_3 6H_2O$, $ZnCl_2$ and $FeSO_4 7H_2O$ were used to obtain Fe^{3+}, Zn^{2+} and Fe^{2+} ions in the aqueous solution. An aqueous solution containing these ions in the appropriate molar proportions ($Fe^{3+}:Fe^{2+}:Zn^{2+} = 2:0{\cdot}9:0{\cdot}1$) was added to 8M NH_4OH solution at room temperature under constant stirring. The pH was adjusted to 10·5. After an hour, aliquot of the reaction mixture was collected for X-ray and EDAX studies. Oleic acid was added to the mixture and the fluid was again stirred for one hour, during which time the pH was kept at 10·5. The fluid was then heated to 90°C for 5 min and cooled to room temperature (2°C/min). The sample was washed a number of times with distilled water and finally washed with acetone. This acetone wet slurry was dispersed in kerosene and heated to 65°C, in order to remove acetone. The sample was solid below 200 K and liquid above this temperature.

The percentage substitution of Zn was verified by EDAX and found to be $9{\cdot}8 \pm 0{\cdot}3\%$. To characterize the formation of single phase spinel structure, X-ray diffraction pattern was recorded using Philips X-ray diffractometer with CuKα radiation. The structure was found to be single phase fcc spinel structure with a lattice parameter of 8·36 A (figure 1). The average particle size was calculated using Scherrer's formula, using the full width at half maximum intensity of the plane (3 1 1) of the pattern. The value thus obtained (after accounting for the instrumental line broadening) was 100 A. The specimen was also examined under AEI Cornith Transmission Electron Microscope (TEM). The particles were found to be almost spherical with

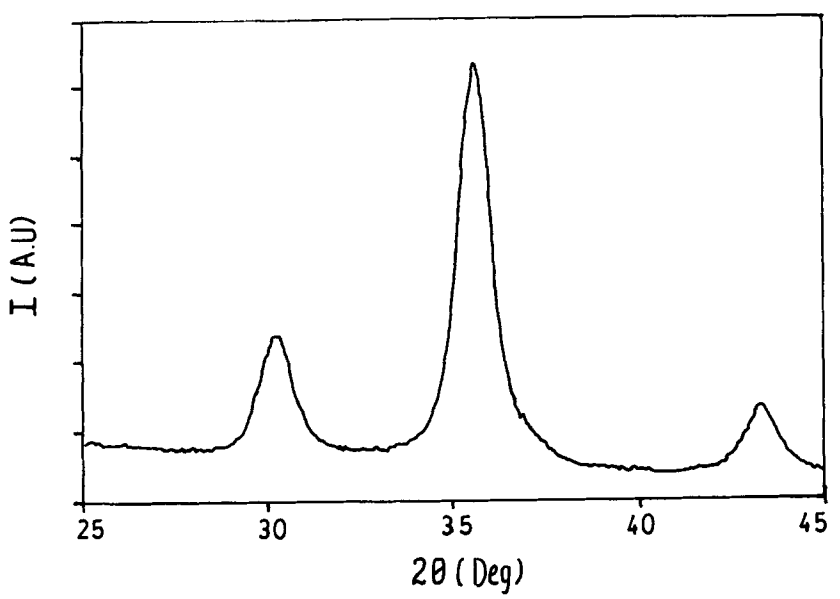

Figure 1. X-ray diffractogram of Zn-substituted ferrite sample (ZFO).

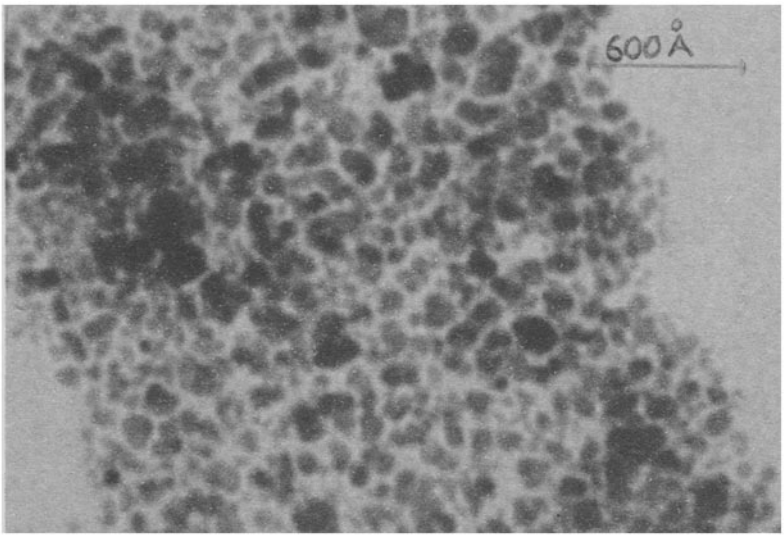

Figure 2a. Electron micrograph of ZFO sample.

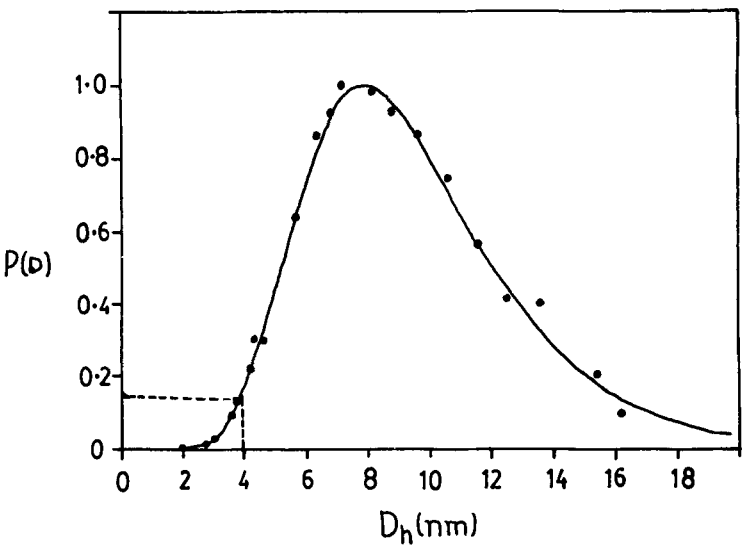

Figure 2b. Particle size distribution for ZFO sample. ● Expt. points. —Log-normal distribution.

average median diameter (Dm) of 90 A and standard deviation (σ) 0·36. Figure 2b shows the particle size distribution pattern using these values.

Room temperature magnetization measurements were carried out using search coil method [18]. Figure 3 shows the reduced magnetization (M/M_s) versus applied field (H) for the $Zn_{0.1}Fe_{0.9}Fe_2O_4$ magnetic fluid (ZFO) at room temperature. To describe

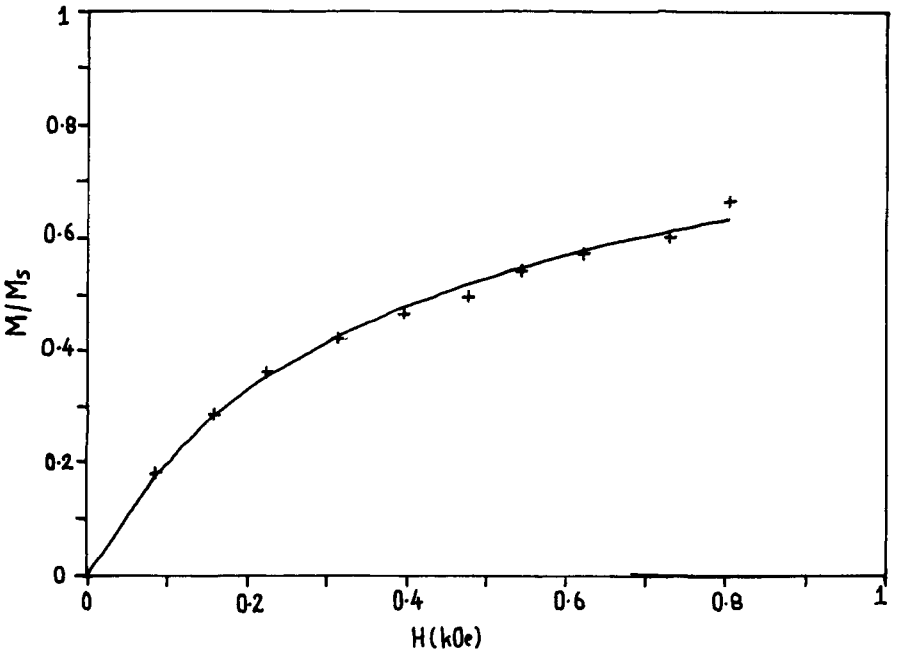

Figure 3. Room temperature M/M_s vs H. Line through the data point is a theoretical fit using $Dm = 98$ Å and $\sigma = 0{\cdot}38$ [19].

the magnetization of the magnetic fluids several theoretical models are being used [19] but the simplest one is Langevin's model. Using this model and our earlier method [20,21] M/M_s was calculated for each value of H. Fit to the data points in figure 3 yielded the values of median diameter, standard deviation, and M_s (saturation magnetization of the fluid) as 98 A, 0·38 and 150 G, respectively.

ESR spectra were recorded using an X-band Bruker ESP-200 spectrometer. A low temperature cryogenic system attached with Bruker ER 4111 temperature controller model was used to vary the temperature from 100 K to room temperature (300 K). The original fluid of 150 G was diluted 10 times in kerosene and two sets of data were recorded. In one set the sample was cooled to 77 K in the residual field of 100 Oe (LFC) while, in the second set the fluid was cooled in 1·1 kOe from room temperature to 77 K. In both cases, the spectra were recorded during the heating cycle. Finally, ESR spectra of coated particles were recorded at 300 K and 77 K.

3. Results and discussion

3.1 *Lineshape analysis*

The conventional approach in analyzing the width and lineshape of a resonance absorption curve is to use either the Lorenzian or Gaussian lineshape. The main difference between these two is, Lorenzian lineshape is slightly sharper in the centre and decreases much more slowly in the wings beyond the half amplitude or first derivative

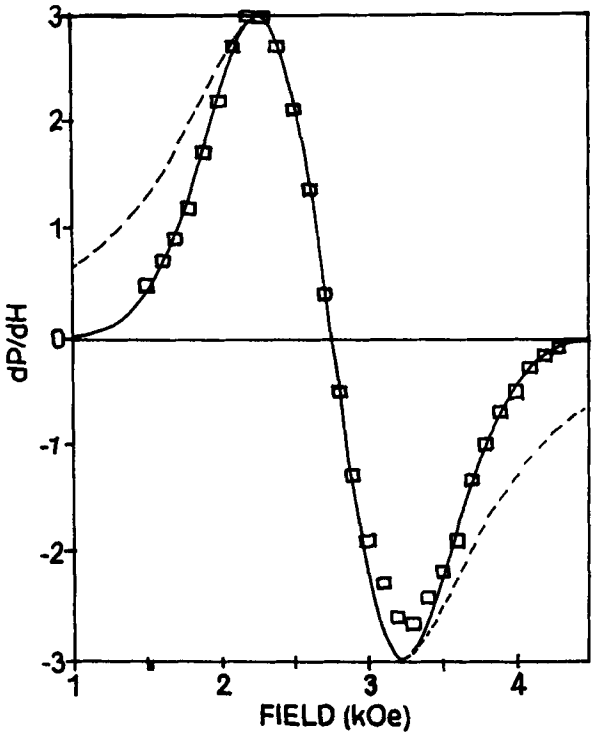

Figure 4. ESR curve of 125 K. - - - Lorentzian fit. ——Gaussian fit. □ expt. points.

points. This can be confirmed by using the value of peak amplitude, A_p, ΔH_{pp} and H_r deduced from experimental resonance curve. Figure 4 shows a resonance curve at 125 K with two different lineshapes. It is evident from the figure that the Gaussian lineshape given by [14],

$$dP/dH = A_p X \exp[-1/2(X^2 - 1)] \tag{1}$$

agrees well with the experimental points, where $X = (H - H_r)/(1/2\Delta H_{pp})$ and H = applied field. Throughout this work we have deduced values of H_r, ΔH_{pp} and A_p from the best fit to the data.

3.2 *Resonance spectra* $T > T_m$

Resonance spectra of the coated powder show an asymmetric line broadening (figure 5) both at 77 K and 300 K. The observed line broadening in the sample may arise due to random orientation of the easy axes, the interparticle dipolar interactions and to unresolved magnetostatics modes. But the spectrum becomes less asymmetric when the same particles are dispersed in liquid carrier like kerosene. This indicates that the deviation of easy axes from the applied field direction are reduced (this is because of Brownian motion of the particles). It was also observed that the line width decreases with dilution (varies from 857 Oe for the most concentrated fluid to 650 Oe for ten times

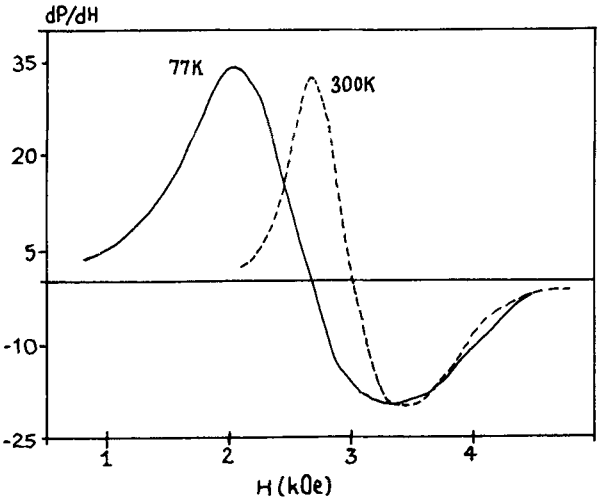

Figure 5. Resonance spectra of coated powder at 300 K and 77 K.

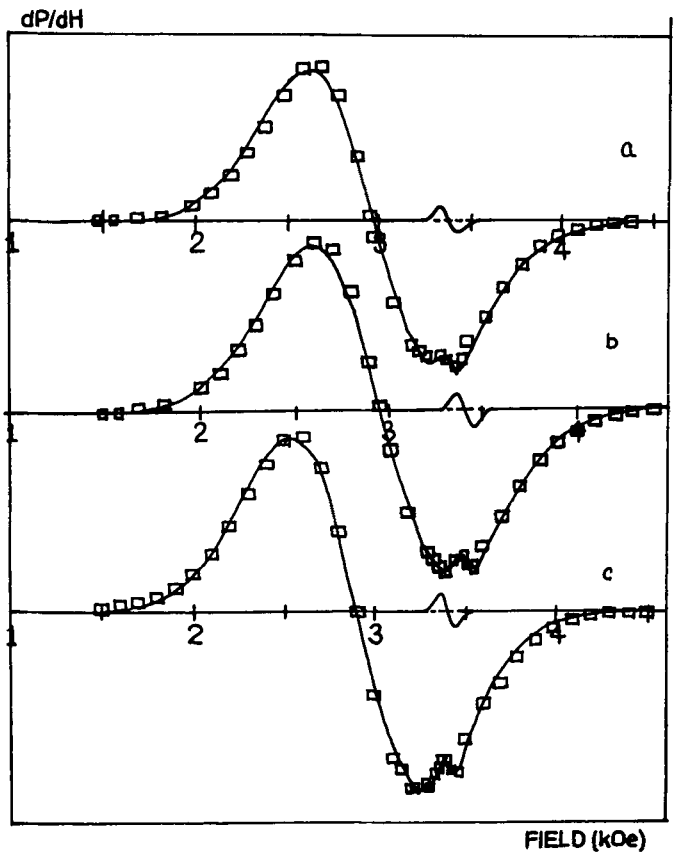

Figure 6. Typical ESR spectra for low field cooled sample ($T > T_m$). —— theoretical points using eq. (1). □ is expt. points (a) 214 K, (b) 235 K, (c) 245 K.

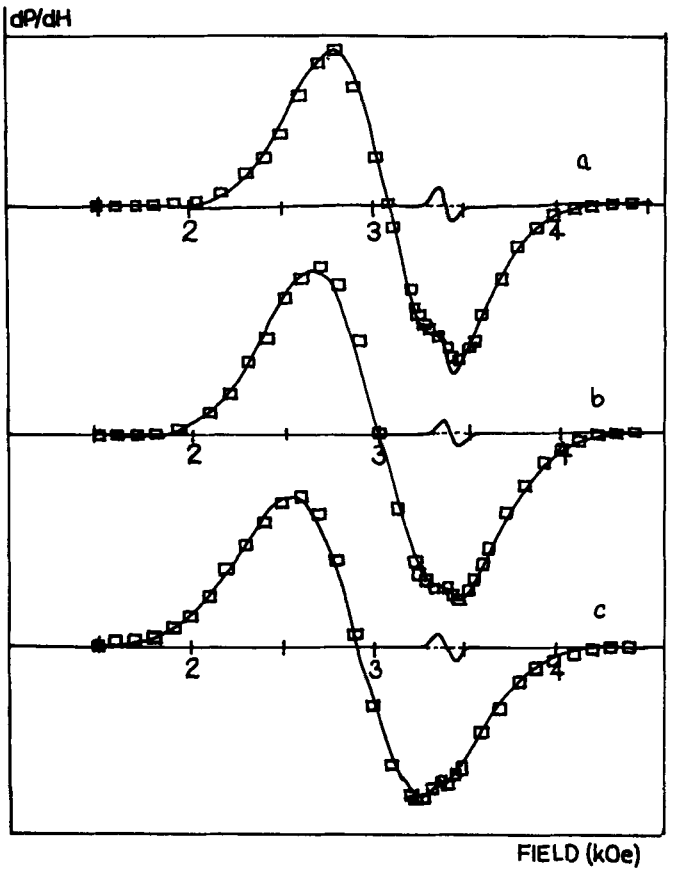

Figure 7. Typical ESR spectra for high field cooled sample ($T > T_m$) (a) 235 K, (b) 265 K, (c) 297 K.

diluted fluid). This decrease in line width may be due to decrease in interparticle dipolar field. Similar behaviour was also observed by Sharma and Waldner [9]. Figures 6 and 7 show some typical ESR spectra for LFC and HFC samples, respectively, for $T > T_m$. In both the cases, an additional narrow line was observed in the vicinity of the minimum. A notable feature in the above spectra is a systematic shift of the kink from left to right of the minima. This kink disappeared below the melting point of the carrier (figures 8 and 9).

Sharma and Waldner [9] observed a narrow line for Fe_3O_4 ferrofluid in a non-aqueous medium. They found [9] that the width of this narrow line is dilution-sensitive. The reason for this observed dilution sensitive width is due to the reduction in interparticle dipolar interaction upon dilution. From the present spectra (figures 6 and 7) it is very difficult to say whether the width of the narrow line is temperature sensitive or not. There are two possible sources which can give a narrow line in ESR spectra; (i) presence of free radicals either in the coating liquid or paramagnetic impurities in carrier liquid and (ii) superparamagnetic resonance because of the presence of very fine

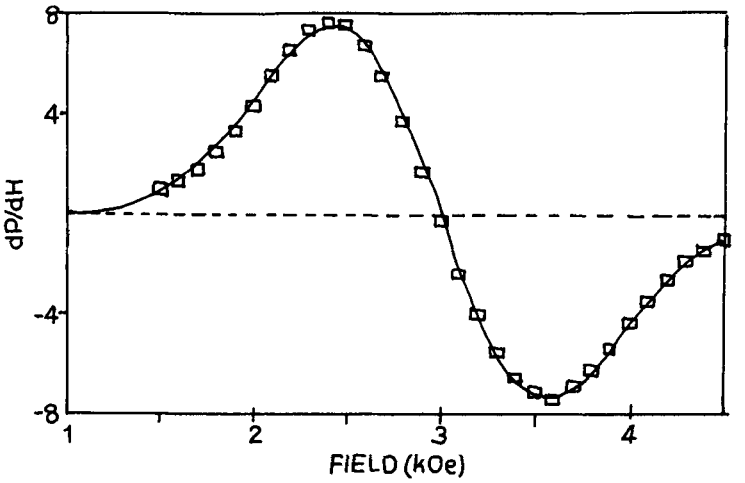

Figure 8. ESR spectra of LFC sample ($T < T_m$) $T = 121$ K.

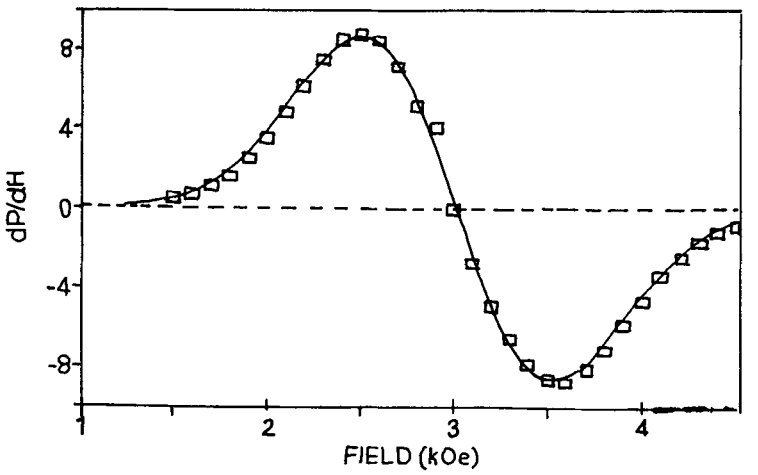

Figure 9. ESR spectra of HFC sample ($T < T_m$) $T = 155$ K.

particles in the system. The ESR spectra of surfactant and carrier show the absence of a narrow line which supports that this line is not due to free radicals or any paramagnetic impurities. Therefore, the only possible reason for this narrow line will be due to very small fraction of very fine particles, which gives superparamagnetic resonance effect at a given temperature and field.

In a magnetic fluid two relaxation mechanisms can occur (i) Brownian rotational diffusion characterized by relaxation time [22],

$$t_B = (3V_h\eta)/kT \tag{2}$$

and (ii) by Neel relaxation with relaxation time [23–24],

$$t_N = t_0(KV/kT)^{1/2}\exp(KV/kT) \quad \text{for} \quad KV/kT > 2 \tag{3}$$

$$= t_0(KV/kT) \quad \text{for} \quad KV/kT \ll 1. \tag{4}$$

where, V_h and V are the effective hydrodynamic and magnetic volumes of the particles, respectively. η is the viscosity of the fluid, K is the anisotropy constant, k is the Boltzmann constant and the pre-exponent factor t_0 has a value of approximately 10^{-9} s. Therefore, the dominant mode of magnetization process of the particle will be that which has the shortest relaxation time. In fact, large particles relax via Brownian rotation while, small particles through Neel rotation [1]. As ferrofluids contain a distribution of particle sizes both mechanism will, in general, contribute to the magnetization for $T > T_m$ with an effective relaxation time [25]

$$t_{eff} = t_N t_B/(t_N + t_B) \tag{5}$$

and superparamagnetic (SP) behavior will be exhibited by those for which t_N is much less than the characteristic Larmor precession time. Aharoni [26] has considered the effect of external magnetic field on SP relaxation time, because the field polarizes the large particles and reduces the size for SP behavior. However, the extremely small particles cannot be quenched unless a very large magnetic field is applied. Therefore, one expects a narrow magnetic resonance signal if a sample contains extremely small particles which are SP state in an applied field, H. Of course the width of the line may further reduce depending upon the viscosity of the fluid (equations 3 and 4).

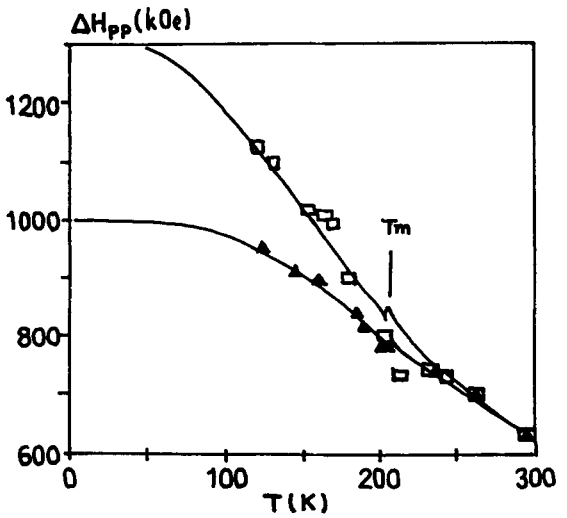

Figure 10. Variation of peak-to-peak line width for LFC (□) and HFC (Δ) samples, Line is fit to the eq. (14). The values used are i) L(LFC) = 1·45 kOe, L(HFC) = 1·0 kOe. ii) $B' = 5 \times 10^{-19}$ erg. iii) $F' = 0{\cdot}5$ K. iv) $KV = 3{\cdot}9 \times 10^{-14}$ erg. v) $Ed = 1{\cdot}4 \times 10^{-18}$ erg. vi) JmH (LFC) = $5{\cdot}2 \times 10^{-17}$ erg. JmH (HFC) = $2{\cdot}62 \times 10^{-14}$ erg [27].

In the case of very small particles, anisotropy energy (KV, where K is an anisotropy constant and V is the volume of the particle) is much smaller than the thermal energy (kT). Therefore the response time of the magnetic moments to random thermal force will be [23]

$$t_{sp} = M_s V/gkT \tag{6}$$

where, M_s is the saturation magnetization, g = gyromagnetic ratio. If this fluctuation is faster than Larmor precession time t_L, effects of magnetocrystalline anisotropy are motionally averaged out roughly by a narrowing factor, $f = t_{sp}/t_L$ which is equal to [9]

$$f = (M_s V H_r)/(2\pi kT). \tag{7}$$

From (7), it is clear that line width of SP resonance would be proportional to the volume of the particles. This is confirmed by Aharoni and Litt [27]. Adopting the procedure of Sharma and Waldner [9] in the present case, the particle size corresponding to the observed line width will be 41 A (neglecting the interparticle dipolar fields) for coated particles which is around 1·2% volume fraction of the particles in the system (this is obtained from particle size distribution curve for the present sample, figure 2b). This agrees with the observed 1% magnitude of SP-phase in comparison with the broad signal. All the above observations are consistent with the presence of small fraction of very fine magnetic particles in the system.

3.3 *Line width analysis*

Experimental points of peak-to-peak line width (ΔH_{pp}) for LFC and HFC configurations are shown in figure 10. The line width increases with decrease in temperature. The observed variation can be explained as follows.

Let us first consider a model of regularly spaced magnetic centres dispersed in a non-magnetic matrix and they are SP particles, i.e. net spin $\Delta nS \gg 0$, where Δn is the net population of spin aligned along the easy axis of magnetization and S is the effective spin of the magnetic centres. Assuming the presence of two level system, one can write the ESR line width as [19]

$$\Delta H_{pp} = L \tanh[\Delta E/2kT] \tag{8}$$

and

$$L = 5g\beta Sn/R^3, \tag{9}$$

where $g = g$-factor, β = Bohr magneton, n = total number of magnetic centres, R = distance between the adjacent particles and E is the energy barrier. Therefore the line width depends upon R and ΔE, which in turn depends on the particular system under study. In the present investigation, we are studying the effect of temperature on the system. Therefore, R remains unchanged and the main contribution to line width will be ΔE term. This makes us to consider the effect of various terms which contributes to ΔE.

As the system is in liquid state above the melting point of the carrier ($T_m \approx 200$ K), one can write ΔE as

$$\Delta E = E_v + E_a + E_m + E_d. \tag{10}$$

The first term in (10) is the energy of Brownian-orientational motion i.e. viscosity energy (E_v), which can be written as

$$E_v = 3\theta\eta V_h, \tag{11}$$

where θ is a coupling constant. As T approaches T_m, the magnetic particles can relax via Brownian rotation in addition to Neel which makes viscosity of the liquid an important parameter. The viscosity study of this fluid (ZFO) indicates that fluid is Newtonian and the change in viscosity with temperature can be described by the Andrade's equation

$$\eta = B\exp[F/\{R_g(T - T_m)\}]. \tag{12}$$

Here, B is a constant. F and R_g are apparent activation energy for the flow and universal gas constant, respectively. Substituting (12) into (11), the viscosity energy is

$$E_v = B'\exp[F'/(T - T_m)], \tag{13}$$

where $B' = 3\theta V_h B$ and $F' = F/R_g$.

The second term, E_a, is simply KV while E_m is JmH, where J is a coupling constant and m is the magnetic moment. Substituting all these values in (10), we can write (8) as,

$$\Delta H_{pp} = L\tanh[(1/2kT)\{B'\exp(F'/(T - T_m)) + KV + JmH + Ed\}]. \tag{14}$$

The line through the data points in figure 10 is the best fit to (12). It was found that KV remains constant for LFC and HFC samples, but JmH changes dramatically (nearly 500 times). This is due to the fact that as the system is frozen in the field of 1·1 kOe, the large number of particles is oriented in the direction of applied field and hence large value of JmH. The decrease in the value of ΔH_{pp} also supports this concept, because for more ordered state the thermal energy required to create a disorder is large. Therefore the line width will remain constant for larger temperature region. This is true for multidomain structure, where the ΔH_{pp} remains nearly constant till the Curie temperature is reached [24]. The observed discontinuity in the curve indicates the effect of viscosity on the line width. A remarkable feature in figure 10 is that above the melting point of the carrier, the variation of line width is the same for LFC and HFC samples, which shows the validity of eq. (5).

4. Conclusion

The present study reveals that (i) A narrow line observed in room temperature and above melting point of the carrier is attributed to a very small volume fraction of particles present in the system. (ii) The percentage of very small particle volume fraction agrees well with particle size obtained from electron micrograph. (iii) Line width increases with decreasing temperature for both low and high field cooled samples.

Acknowledgements

Authors are thankful to Dr S W Charles, Department of Chemistry, UCNW, Bangor, UK for providing experimental facilities. They are also thankful to UGC and British Council for ALIS programme and DST for financial assistance.

References

[1] S W Charles and J Popplewell, in *Ferromagnetic materials*, Edited by E P Wohlfarth (North Holland, Amsterdam, 1980) **2**, 509
[2] S D Bhagat and R V Mehta, *Indian J. Pure Appl. Phys.* **30**, 84 (1992)
[3] K O'Grady, J Popplewell and S W Charles, *J. Magn. Magn. Mater.* **39**, 56 (1983)
[4] A E Berkowitz, J A Lahut and C E Van Buren, *IEEE Trans. Magn.* **16**, 184 (1980)
[5] A Tari, J Popplewell and S W Charles, *J. Magn. Magn. Mater.* **15–18**, 1125 (1980)
[6] M El-Hilo, K O'Grady and R W Chantrell, *J. Magn. Magn. Mater.* **114**, 295, 307 (1992)
[7] A E Berkowitz, J A Lahut, I S Jacobs and L M Levinson, *Phys. Rev. Lett.* **34**, 594 (1975)
[8] J Tajada, X X Zhang and L Balcells, *J. Appl. Phys.* **73**, 6709 (1993)
[9] V K Sharma and F Waldner, *J. Appl. Phys.* **48**, 4298 (1977)
[10] S P Vaidya, R V Mehta and J M Patel, *Physics of magnetic materials*, Edited by M Takahashi *et al* (World Scientific, 1987) 350
[11] A L Tronconi, P C Moraris, F Pelegrini and F A Tourinho, *J. Magn. Magn. Mater.* **122**, 90 (1992)
[12] K Nagata and A Ishihara, *J. Magn. Magn. Mater.* **104–105**, 1571 (1992)
[13] G M Sutaria, R V Upadhyay and R V Mehta, *J. Colloidal Interface Sci.* **155**, 152 (1993)
[14] T Miahara and K Wawakauri, *IEEE Trans. Magn.* **MAG-23**, 2877 (1987)
[15] G Xiao and C L Chien, *J. Appl. Phys.* **61**, 3308 (1987)
[16] C Hayashi, *J. Vac. Sci. Technol.* **A5**, 1375 (1987)
[17] V Pillai, P Kumar and D O Shah, *J. Magn. Magn. Mater.* **116**, L299 (1992)
[18] M I Shliomis, A F Pshenichnikov, K I Morozov and I Yu Shurubor, *J. Magn. Magn. Mater.* **85**, 40 (1990)
[19] R V Upadhyay and R V Mehta, *Pramana – J. Phys.* **41**, 429 (1993)
[20] W F Brown, *J. Appl. Phys.* **34**, 1319 (1963)
[21] W F Brown, *Phys. Rev.* **130**, 1677 (1963)
[22] L Neel, *Ann. Geophys.* **5**, 99 (1949)
[23] M I Shliomis, *Sov. Phys. USP* **17**, 53 (1974)
[24] A Ahroni, *Phys. Rev.* **177**, 793 (1969)
[25] S M Ahroni and M H Litt, *J. Appl. Phys.* **42**, 352 (1971)
[26] P C Moris, M C L Lara and K S Neto, *Philos. Mag. Lett.* **55**, 181 (1987)
[27] These values are in good agreement with the reported values of K and F using particle diameter of 90 Å. The value of K was found to be $1{\cdot}0 \times 10^5$ erg/cc and the value of F was 4 kCal/Mole [13]