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Journal of Magnetism and Magnetic Materials 201 (1999) 73–76

Journal of magnetism and magnetic materials

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Electron spin resonance investigation of Mn–Zn ionic ferrofluid

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Received 12 May 1998; received in revised form 7 September 1998

Abstract

Electron spin resonance measurements are analysed for Mn–Zn ionic ferrofluid. The temperature dependence of the field-cooled samples resonance field exhibits two distinct region for $T > 40$ K and $T < 40$ K. The former is interpreted in terms of uniaxial anisotropy energy contribution to the resonance field while the later is interpreted as due to surface spin freezing in the direction of DC-magnetic field.

Keywords: Ionic ferrofluids; ESR

1. Introduction

Electron spin resonance (ESR) technique has proved to be a boon companion of modern material research. The technique helps us to probe the type of processes that may take place in materials via the interactions of magnetic moment generated due to unpaired electron with its neighbouring as well as more distant environment [1]. In the field of ferrofluids too the technique is gradually gaining importance [2–7]. Recently this technique was used to characterise surfacted ferrofluid involving Mn–Zn ferrite particles [7]. The Mn–Zn fluid synthesize was found to be temperature sensitive with low Curie temperature [8]. Variation of line width with temperature revealed that the spectra are the resultant of two phases viz. ferrimagnetic and superparamagnetic and the relative contribution of superparamagnetic fraction increases from 5% to 60% as the temperature increases from 200 to 300 K [7]. Similar study of ionic ferrofluid containing Mn–Zn ferrite particles is reported in this paper.

2. Synthesis of ionic ferrofluid

Massart's method was used to synthesize the fluid [9]. $Mn_{0.5}Zn_{0.5}Fe_2O_4$ particles were coprecipitated and the adsorbed counter ions (Na, OH, etc) were removed by HNO_3. Stable cationic

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0304-8853/99/$ - see front matter
PII: S0304-8853(99)00038-4

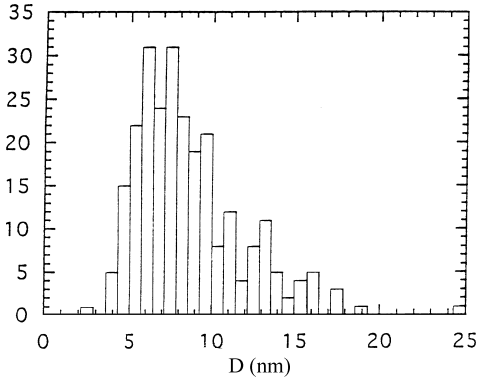

Fig. 1. Histogram obtained from TEM for ionic ferrofluid.

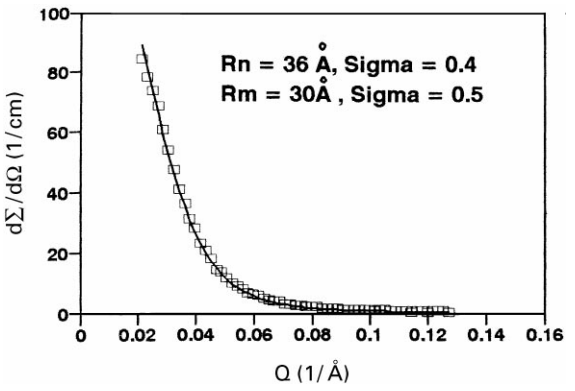

Fig. 2. SANS pattern of ionic ferrofluid at 300 K.

ferrofluid was prepared by first treating the particles with ferric nitrite. The X-ray diffraction pattern of the particles showed that the particles are having spinel structure. Using (3 1 1) plane the particle size was calculated as 83 Å. The size and size distribution were also determined from TEM. The median diameter of lognormal size distribution function was found to be 78 Å with a standard deviation $\sigma = 0.34$. The histogram is shown in the Fig. 1. The chemical composition of the particle was ascertained by atomic mass absorption spectra. The ratio of Fe/Mn and Fe/Zn was found to be greater than 4 (5.9 and 5.2, respectively). This indicates loss of Zn and Mn ions during the synthesis. The loss may create a lattice vacancy or one can have a defected spinel structure. This will lead to modification of magnetic properties of the particles like, domain magnetisation, M_d, and Curie temperature, T_c, pyromagnetic co-efficient, anisotropy, etc. Hence both the small-angle neutron scattering (SANS) pattern as well as ESR spectra of this ionic ferrofluid will be quite different compared to that of surfacted ferrofluid.

3. Small-angle neutron scattering study at 300 K

SANS pattern was recorded at the spectrometer installed at CIRUS, Bhabha atomic Research Centre, Trombay. The data points are shown in the Fig. 2. The theoretical line was generated using the following procedure.

SANS experiment measures the coherent differential scattering cross-section $d\Sigma/d\Omega$ as a function of Q, ($= 4\pi/\lambda \sin\theta$, and θ is the scattering angle). For a dilute polydispersed dispersion it is shown that [8]

$$d\Sigma/d\Omega = n(\rho_p - \rho_s)^2 \int V^2(R) f(R) P(Q,R)\, dR\,, \quad (1)$$

where n is the particle number density, V is the volume of the particle and ρ_p and ρ_s are the scattering length densities of the particle and the solvent, respectively. $P(Q)$ is the particle form factor and $f(R)$ is the size distribution function. For ferrofluid the form factor is calculated assuming spherical particles and log-normal size distribution. For unpolarized neutron beam and in zero field (1) can be written as

$$(d\Sigma/d\Omega)_{tot} = (d\Sigma/d\Omega)_n + 2/3(d\Sigma/d\Omega)_M\,, \quad (2)$$

where

$$(d\Sigma/d\Omega)_n = n(\rho_{pn} - \rho_{sn})^2 \int V^2(R_n) f(R_n) P(Q,R_n)\, dR_n \quad (3)$$

and

$$(d\Sigma/d\Omega)_M = n(\rho_{pm})^2 \int V^2(R_M) f(R_M) P(Q,R_M)\, dR_M \quad (4)$$

where the suffixes n and M stand for nuclear and magnetic contributions, respectively. By incorporating appropriate values of the parameters the theoretical curve was generated. In the calculation, 80% magnetic contribution was considered at room temperature. This contribution is higher than that for surfacted ferrofluid (i.e. 40% [8]). The nuclear size and standard deviation, σ, agree well with those obtained from TEM data.

The SANS results confirm that for ionic ferrofluid the increase in magnetic contribution at room temperature indicates the change in cationic distribution of the particle (in comparison with surfacted fluid) and thus increases in the Curie temperature of the particle. Further it also indicates that the surface modification increases the thickness of the surface layer which in turn results in to decrease of magnetic radius by 6 Å (which is only 3 Å for surfacted fluid). The above conclusions are corroborated by ESR measurements.

4. ESR measurements

ESR measurements were carried out on Varian E102 spectrometer operated at 9.26 GHz. The samples cooled in a magnetic field (1.5 T) are referred as 'field-cooled' (FC) samples and those without field are referred as 'zero field-cooled' (ZFC) samples.

ESR spectra of ZFC samples were recorded at different temperatures and were found to be isotropic. The line width was found to decrease with increase in temperature. It is known that in a randomly oriented dispersed ferromagnet the absorption line width turns out to be a non-monotonic function of temperature. At low temperature the line width is large due to the scatter in direction of anisotropic field of particles (inhomogeneous broadening). As the temperature increases the tendency to make magnetic moment isotropic causes line width to decrease.

ESR spectra of FC samples were found to be anisotropic and spectra at different temperature were recorded for parallel and perpendicular geometries. Each spectra were fitted to Gaussian line profile and resonance field, line width and amplitude were deduced. Fig. 3 shows the variation of resonance field with temperature. Correction

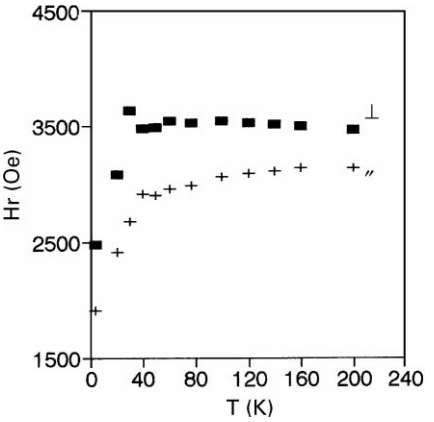

Fig. 3. H_r variation with temperature.

due to variation of line width with temperature was taken into consideration while deducing resonance field (H_r). For both the geometries there arises two distinct regions (i) for $T > 40$ K and (ii) $T < 40$ K.

The behaviour for $T > 40$ K can be explained as follows. It is known that dependence of uniaxial anisotropy energy on temperature is similar to that of magnetostatic i.e demagnetisation energy. Thus H_r ($\|$) will increase with temperature while H_r ($\perp$) will decrease with temperature. The difference ΔH_r (i.e. H_r ($\|$) $- H_r$ ($\perp$)) yields the anisotropy constant K, which was found to be 10^5 erg/cc. This value is higher than the bulk values. This result further supports our conclusion that the treatment of ferric nitrate on the ferrite particles modifies the cation distribution resulting in increase in anisotropy.

The decrease of resonance field for $T < 40$ K is intriguing. We try to explain this behaviour on the line similar to that suggested by Kodam et al. [10]. Below 40 K the surface spin freezes and they freeze in the direction of DC-magnetic field. This yield an exchange coupling between the surface and core spins. This give rise to an 'Unidirectional' anisotropy with easy axis in the direction of the field. As a result there is a sudden drop in parallel resonance field below 40 K, while for perpendicular resonance field the freezing of surface spin and coupling between surface and core increases the magnetization of the sample, which in turn decrease the resonance field.

Acknowledgements

The work has been carried out under IFCPAR (CEFIPRA) Project No. 1508-2 and IUC-DAEF Project No. PB36.

References

[1] C.S. Sunandana, Bull. Meterol. Sci. 21 (1998) 1.
[2] V.K. Sharma, F. Waldner, J. Appl. Phys. 48 (1977) 4298.
[3] K. Nagat, A. Ishihara, J. Magn. Magn. Mater 105 (1992) 1571.
[4] R.V. Upadhyay, D. Srinivas, R.V. Mehta, P.M. Trivedi, Pramana-J. Phys. 45 (1995) 419.
[5] M.D. Sastry, Y. Babu, P.S. Goyal, R.V. Mehta, R.V. Upadhyay, D. Srinivas, J. Magn. Magn. Mater. 149 (1995) 64.
[6] Y.U. Raikher, V.I. Stepanov, Phys. Rev. B 50 (1994) 6250.
[7] R.V. Upadhyay, R.V. Mehta, D. Srinivas, K.H. Parekh, T. Upadhyay, in: J. Tani, P.F. Gobin (Eds.), Proceedings of the Japan–France Seminar on IMS, Sendai, Japan, 1997, p. 83.
[8] T. Upadhyay, R.V. Upadhyay, R.V. Mehta, V.K. Aswal, P.S. Goyal, Phys. Rev. B 55 (1997) 5585.
[9] R. Massart, C. R. Acad. Sci. Paris, Ser. C 291 (1980) 1.
[10] R.H. Kodama, A.E. Berkovitz, E.J. McNiff, Jr., S. Foner, J. Appl. Phys. 81 (1997) 5552.