Experimental evidence of dimer disruption in ionic ferrofluid: a ferromagnetic resonance investigation

P.C. Morais[a,*], G.R.R. Gonçalves[a], A.F. Bakuzis[a], K. Skeff Neto[a,b], F. Pelegrini[c]

[a]*Instituto de Física, Universidade de Brasília, Núcleo de Física Aplicada, C.P. 004455, Campus Universitario, CEP 70919-970, Brasília-DF, Brazil*
[b]*FINATEC, Fundação de Empreendimentos Científicos e Tecnológicos, CEP 70910-900, Brasília–DF, Brazil*
[c]*Instituto de Física, Universidade Federal de Goiás, C.P. 131, CEP 74001-970, Goiânia-GO, Brazil*

Abstract

Ferromagnetic resonance was used to investigate the thermal disruption of dimers in nickel ferrite-based ionic ferrofluid. The data were analyzed using four resonance lines, assigned to monomers and dimers. The resonance field shift around 280 K indicates the frozen-to-liquid state transition. Above 290 K, however, the dimer resonance field shows a critical behavior closely related to a second-order phase transition. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Ferromagnetic resonance has been successfully used to investigate ionic [1], surfaced [2], and biocompatible [3] ferrofluids (FFs). From a fundamental standpoint, ferromagnetic resonance has been used to understand, for instance, the surface charge–discharge process [4], the magnetic particle–particle interaction [5], the magnetic anisotropy [6,7], the exchange field [8], and the Brownian relaxation [9] in ionic FFs, using the magnetic nanoparticle itself as the resonant center. On the other hand, magnetic resonance has been traditionally used to investigate structural phase

transitions [10] as well as molecular dynamics [11], through the analysis of the resonance line structure as a function of the temperature. The temperature dependence of the resonance line splitting is usually proportional to the order parameter associated to a phase transition [10] or alternatively it may describe the temperature dependence of more complex molecular dynamics [11].

Despite of many experimental evidences of line structure in the ferromagnetic resonance spectra of FFs, all the investigations performed to date have been focused on the linewidth and on the resonance field obtained from the envelope resonance line [1–9]. As a consequence, important details such as dimer formation in FFs [12] have been neglected. In this study, a new methodology was applied to the analysis of the ferromagnetic resonance envelope line in terms of several components, from which important information relating to the

*Corresponding author. Tel.: + 55-61-2736655; fax: + 55-61-2723151.

E-mail address: pcmor@fis.unb.br (P.C. Morais).

temperature dependence of dimer disruption is obtained. From the fundamental point of view, the resonance data presented here may help to understand the influence of the temperature upon the particle organization pattern in FFs. Computer simulation suggests that particle–particle interaction in surfaced FFs, containing large-sized particles (about 15 nm in diameter), lead to the formation of rings and open structures under moderate magnetic fields, while under stronger magnetic fields the complex structures break up to form chains [13]. Finally, a recent investigation using ionic FFs strongly supports the important contribution of the dimer structure to the static birefringence signal, even at near-zero-field condition [14].

2. Experiment and discussion

The ionic nickel ferrite ($NiFe_2O_4$) FF sample used in this work was chemically synthesized by coprecipitating Ni (II) and Fe (III) ions in alkaline medium, following passivation and peptization of the oxide nanoparticles in water, as described in the literature [15]. The particle-size distribution obtained from transmission electron microscopy follows the typical lognormal profile with a particle diameter of 10.3 ± 0.1 nm and size dispersion of 0.38 ± 0.01. The resonance spectra were taken using a commercial Bruker ESP200 X-band spectrometer tuned around 9.43 GHz. Particle concentration was fixed at about 2.5×10^{16} cm^{-3} to reduce particle–particle interaction [5]. Fig. 1 shows typical ferromagnetic resonance spectra of the FF sample at 300 K. In the upper frame of Fig. 1 the first derivative of the absorption spectrum clearly shows that different magnetic structures are present. The multiplicity on the envelope resonance line, however, is much more evident in the lower frame of Fig. 1, using the second derivative of the absorption spectrum. Though a visual inspection of the spectra in the lower frame of Fig. 1 suggests the convolution of three single resonance lines, a detailed numerical analysis supports the convolution of four resonance lines instead. In the upper frame of Fig. 2 the thick black line represents a typical resonance spectrum of the field-frozen FF sample whereas the thinner white line (inside the
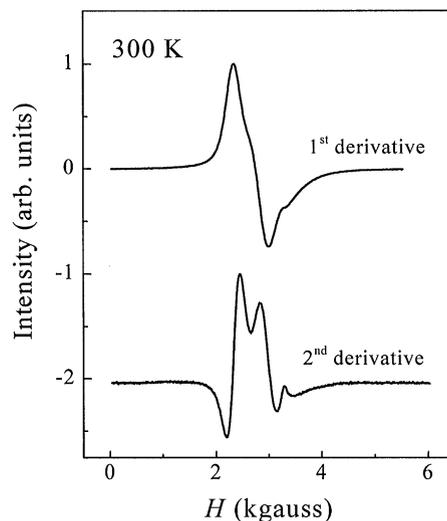

Fig. 1. Typical ferromagnetic resonance spectra of nanomagnetic particles. The first derivative spectrum is shown in the upper frame while the corresponding second derivative spectrum is shown in the lower frame.
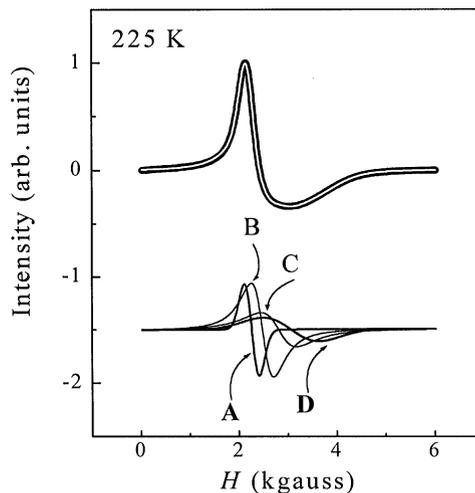

Fig. 2. In the upper frame the thick black line represents the experimental data whereas the thinner white line (inside the black line) represents the best fit using four components. The resonance components (A, B, C, and D) are shown in the lower frame.

black line) represents the best fit using four components. Increasing the resonance field values the four components shown in the lower frame of Fig. 2 are Gaussian (A), Lorentzian (B), Lorentzian (C) and

Gaussian (D). Symbols in Fig. 3(a) represent the temperature dependence of the resonance field associated to each one of the single resonance lines (H_R^A, H_R^B, H_R^C, and H_R^D), according to the numerical analysis described below. In Fig. 3(b) open and full circles represent the temperature dependence of the line splitting ($H_R^D - H_R^B$) and ($H_R^D - H_R^C$) in the temperature range of 290–340 K, respectively.

The identification of each one of the single resonance lines resulting from the deconvolution procedure is a quite difficult task. Nevertheless, a recent analysis based on angular variation measurements of the field-frozen FF samples provided the best strategy to identify the resonance line with a particular magnetic entity [16]. The resonance lines A and D were associated, respectively, to large- and small-sized monomers, while the resonance lines B and C were associated to dimers. The two types of dimers are claimed to be due to the fanning and coherent coupling of medium-sized nanoparticles. This view is strongly supported by the recent analysis of the zero-field birefringence data in ionic FFs [14]. Analysis of the data in Fig. 3(a) shows that the resonance field shift observed around 280 K, for all resonance components, is more likely due to the transition of the aqueous-based FF sample from the solid to the liquid state. However, the resonance field shift associated to the resonance lines B and C around 340 K [see Fig. 3(a)] is more likely due to the thermal disruption of the dimer. Note from Fig. 3(a) that no significant resonance field shift is observed for the resonance lines A and D around 340 K. Furthermore, we found that the intensity of the resonance lines B and C decreases as the temperature increases above 280 K. This is a clear indication that dimer disruption takes place at high enough temperatures, thus reducing the resonance signal due to the medium-sized magnetic structures, from which dimers are built. Such resonance data are consistent with the reduction of the zero-field birefringence in ionic γ-Fe_2O_3 and $MnFe_2O_4$ FFs as the temperature is raised above 320 K [17]. The orientation of the magnetic moments of the particles in the dimer structure about the direction of the external applied field may cause the resonance line to be changed from a gaussian-shaped curve to a Lorentzian-shaped one. A narrowing factor proportional to $|\cos^2\psi - 1|$, where ψ is the bond angle between the line connecting the two particles in the dimer and the external field, may account for the lineshape change [18].

In order to perform a quantitative analysis of the temperature dependence of the resonance line splitting ($H_R^D - H_R^B$) and ($H_R^D - H_R^C$) one needs to
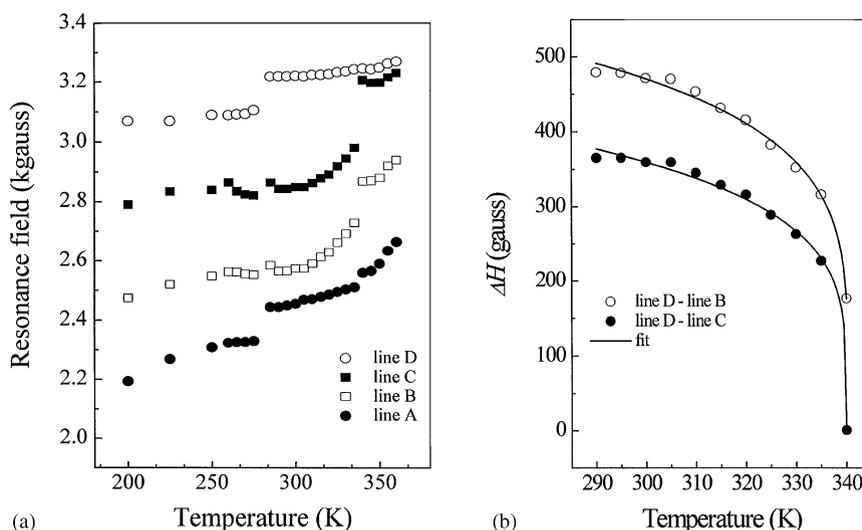

Fig. 3. Symbols in (a) represent the temperature dependence of the resonance field of each one of the single resonance lines (A, B, C, and D) while in (b) open and full circles represent the temperature dependence of the line splitting ($H_R^D - H_R^B$) and ($H_R^D - H_R^C$), respectively.

introduce the dimer picture and the corresponding magnetostatic energy term

$$U_{ms} = -\beta(\mu^2/R_0^3)[2\cos(\theta_i - \psi)\cos(\theta_j - \psi)$$
$$- \sin(\theta_i - \psi)\sin(\theta_j - \psi)],$$

where β is the dimer coupling parameter, R_0 is the particle–particle equilibrium distance in the dimer structure, and θ_i (θ_j) is the angle between the external field and the magnetic moment of the particle i (j). As far as the dimer structure is concerned, only the two lowest energy configurations need to be included in a first approximation, namely, the fanning (F-mode) and the coherent (C-mode) corresponding to $\theta_i = -\theta_j = \theta$ and $\theta_i = \theta_j = \theta$, respectively [19]. Finally, the dimer coupling parameter (β) seems to hold the key towards a more deep understanding of the resonance field splitting. We first argue that dimers do exist at the expense of a delicate energy balance involving opposite tendencies. Magnetic interaction energy (MI) holds the two particles together while electrostatic interaction energy (EI) and thermal energy work together to take the two particles apart. A difference between ionic and surfaced FFs emerges right from the beginning, since repulsive energy among particles varies with $R_0^{-\alpha}$, α being higher in surfaced FFs. Therefore, identical magnetic particles might be brought closer together when dispersed as ionic FFs than when dispersed as surfaced FFs, thus allowing for different levels of magnetic interaction. Recently, the dimer coupling parameter (β), describing the repulsive–attractive balance, has been identified as the order parameter describing the dimer disruption [14,17]. Second, as far as the resonance data are concerned, one observes the resonance line splitting (ΔH) going critically down to zero at a characteristic temperature (T_c), while showing a first derivative ($d(\Delta H)/dT$) with a divergent behavior as one approaches T_c from below ($T < T_c$). In other words, close to T_c the resonance field splitting may track the dimer disruption, thus suggesting the presence of a second-order phase transition, traditionally described by the Landau theory [20].

In fact, the square value of the resonance line splitting (ΔH^2) has been widely used as the order parameter to follow phase transitions [10]. Thus, it is physically reasonable to associate the square of the resonance line splitting with the order parameter describing the dimer disruption at a particular phase transition temperature (T_c), namely, $\Delta H = A(1 - T/T_c)^\eta$. Inclusion of ΔH^2 as the order parameter, on phenomenological grounds, opens up the opportunity to improve the understanding of the temperature dependence of the resonance line splitting in FFs. The solid and dashed lines in Fig. 3(b) describe the effect of the temperature dependence of the resonance line splitting $\Delta H = A(1 - T/T_c)^\eta$ upon the solid and open symbols, respectively. The best numerical fit gives $T_c = 340.2 \pm 0.1$ K and $\eta = 0.21 \pm 0.01$, strongly supporting the picture of a second-order phase transition associated to the dimer disruption.

Besides the fundamental aspects related to the energy balance involved in magnetic chain-like structure formation and the corresponding disruption into the nanoparticle units at a particular temperature, the practical interest is immediately recognized. The response of a nanomagnetic-based structure to an external magnetic field depends upon the magnetic susceptibility of such a structure, which in turn is sensitive to the particle characteristics, number of particles, and the way the particles are spatially arranged [21]. Therefore, the field and the temperature dependence of the magnetic susceptibility play a key role in the efficiency of many processes based on the magnetic response of nanosized systems, as for instance in magnetothermocytolysis. Investigation of nanomagnetic cluster formation/disruption provides very useful information for the engineering of ferrofluid-based materials of highest magnetic susceptibility at a given value of the external field and temperature range.

3. Conclusion

In summary, this study provides very useful information concerning the use of the magnetic resonance to investigate the nature and geometry of magnetic structures (monomer and dimer) in ionic FFs. The resonance lines A and D occurring at lower and higher resonance fields are associated with large- and small-sized spherical monomers,

respectively. The resonance lines B and C, however, are associated with dimers build up from spherical mid-sized nanoparticles. The difference in resonance field between dimer and monomer, here assigned as the resonance line splitting, shows a temperature dependence closely related to a second-order phase transition. Such a critical behavior is claimed to describe the thermal disruption of the dimer structure, in very good agreement with recent birefringence experiments described in Refs. [14 and 17].

Acknowledgements

References

[1] A.L. Tronconi, P.C. Morais, F. Pelegrini, F.A. Tourinho, J. Magn. Magn. Mater. 122 (1993) 90.

[2] I. Hrianca, I. Malaescu, F. Claici, C.N. Marin, J. Magn. Magn. Mater. 201 (1999) 126.

[3] M.F. Da Silva, F. Gendron, J.C. Bacri et al., in: U. Hafeli, W. Schutt, J. Teller, M. Zborowski (Eds.), Scientific and Clinical Applications of Magnetic Carriers, Plenum Press, New York, 1997, p. 171.

[4] P.C. Morais, F.A. Tourinho, G.R.R. Gonçalves, A.L. Tronconi, J. Magn. Magn. Mater. 149 (1995) 19.

[5] P.C. Morais, M.C.F.L. Lara, A.L. Tronconi et al., J. Appl. Phys. 79 (1996) 7931.

[6] A.F. Bakuzis, P.C. Morais, F.A. Tourinho, J. Magn. Reson. A 122 (1996) 100.

[7] J.F. Saenger, K. Skeff Neto, P. C. Morais et al., J. Magn. Reson. 134 (1998) 180.

[8] A.F. Bakuzis, P.C. Morais, F. Pelegrini, J. Appl. Phys. 85 (1999) 7480.

[9] P.C. Morais, A.L. Tronconi, F.A. Tourinho, F. Pelegrini, Solid State Commun. 101 (1997) 693.

[10] P.C. Morais, G.M. Ribeiro, A.S. Chaves, Solid State Commun. 52 (1984) 291.

[11] P.C. Morais, G.M. Ribeiro, A.S. Chaves, J. Phys. Soc. Jpn. 57 (1988) 2812.

[12] V.M. Buzmakov, A.F. Pshenichnikov, J. Colloid Interface Sci. 182 (1996) 63.

[13] R.W. Chantrell, A. Bradbury, J. Popplewell, S.W. Charles, J. Appl. Phys. 53 (1982) 2742.

[14] A.F. Bakuzis, M.F. Da Silva, P.C. Morais et al., J. Appl. Phys. 87 (2000) 2497.

[15] R. Massart, IEEE Trans. Magn. 17 (1981) 1247.

[16] G.R.R. Gonçalves, A.R. Pereira, A.F. Bakuzis et al., J. Magn. Magn. Mater. 226–230 (2001), in press.

[17] A.F. Bakuzis, M.F. Da Silva, P.C. Morais, K. Skeff Neto, J. Appl. Phys. 87 (2000) 2307.

[18] J.G. Powles, B. Carazza, Magnetic Resonance, Plenum, New York, 1970.

[19] B.D. Cullity, Introduction to Magnetic Materials, Addison-Wesley, London, 1972.

[20] J.-C. Tolédano, P. Tolédano, The Landau Theory of Phase Transitions, World Scientific, Singapore, 1987.

[21] K. Skeff Neto, A.F. Bakuzis, A.R. Pereira, P.C. Morais, J. Magn. Magn. Mater. 226–230 (2001), in press.