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Evidence of reentrant behavior in nanoparticles of ferrite in ferrofluids

D. Zins[a], K. Nakatsuka[b], F. Gendron[c,*], M. Rivoire[c]

[a] *LI2C- colloïdes magnétiques, Université P. et M. Curie, case 75, 4 place Jussieu, 75252 Paris Cedex 05, France*
[b] *Graduate School of Engineering, Tohoku University, Aoba, Aramaki, Aiba-ku Sendai City, 980 Japan*
[c] *Laboratoire des Milieux Désordonnés et Hétérogènes, Université Pierre et M. Curie, Tour 13, Boite 86 case 86, 4 place Jussieu, 75252 Paris Cedex 05, France*

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Abstract

Ferrofluids made up of mixed ferrite particles $Mn_{1-x}Zn_xFe_2O_4$ mono-dispersed in glycerol have been studied by ferromagnetic resonance (FMR) in X band and by magnetization measurements in the temperature range of 3.5–300 K. FMR spectra have been recorded on field-cooled samples. Some features of these spectra are typical of a transition from ferro to spin-glass state, i.e. a reentrant behavior. By taking relaxation into account in the frame of Landau Lifchitz formalism, the freezing temperature $T_f = 40$ K was accurately determined, in good agreement with temperature measurements of the static magnetic susceptibility of field-cooled ferrofluid samples.

Keywords: Ferrofluids; Ferromagnetic resonance; Spin glass; Disordered magnetic spinel

1. Introduction

This paper focuses on ionic ferrofluids made up of mixed ferrite particles $Mn_{1-x}Zn_xFe_2O_4$. We have studied the magnetic resonance properties of these particles after inducing a magnetic texture by applying a magnetic field during the freezing of the liquid carrier. We shall insist on the influence of the chemical composition on the magnetic anisotropy and on magnetization as a function of temperature.

2. Experiments and results

We have performed ferromagnetic resonance (FMR) and magnetization measurements on two types of ionic ferrofluids (F1, F2) made up of mixed ferrite particles $Mn_{1-x}Zn_xFe_2O_4$ mono-dispersed in glycerol with a weight concentration $c = 10^{-3}$. MnZn ferrite particles are prepared by coprecipitation of aqueous solutions of $MnCl_2$, $ZnCl_2$ and $FeCl_3$ mixtures in an alkaline medium. To obtain sufficient electrostatic repulsion between particles, surface treatment and stabilization procedures developed for manganese and cobalt ferrite fine particles [1] were used to prepare manganese–zinc ferrite ionic ferrofluids. Two kinds of particles (P1,

* Corresponding author. Tel.: + 33-01-44-27-44-40; fax: + 33-01-44-27-38-54.
E-mail address: gendron@ccr.jussieu.fr (F. Gendron)

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P2) were synthesized by this chemically soft method with respectively $x_1 = 0.5$ and $x_2 = 0.63$. The mean diameters are respectively, 9.5 and 7 nm. The derivative absorption spectra were recorded at the X band (9.25 Ghz) in the temperature range 3.5–200 K. To freeze the position of particles and to texture the media, ferrofluids were cooled under the fusion point of glycerol in an applied magnetic field of 16 kOe.The magnetic DC field H_{DC} is oriented successively parallel ($\|$) and perpendicular ($\perp$) to the field cooling direction.

We observed only one resonance mode whose position shifts toward the low magnetic field with decreasing temperature, this being notably accentuated for $T < 50$ K. Simultaneously, the linewidth increases from the range 200–400 Oe to the range 1600–2000 Oe with a little narrowing for 3.5 K $< T <$ 20 K. The spectra are not the same as those which are expected in field-oriented spherical particles with a cubic magnetic anisotropy. In fact, the angular variation spectra show the magnetic anisotropy of real dispersed particle systems to be uniaxial. On the other hand, because of the broad linewidth we have observed, we had to taken into account the relaxation phenomena to treat the microwave absorption theoretically. We have used the Landau–Lifchitz formalism [2] and assumed that the absorption spectra result from superposition of those of identical ellipsoid particles (with same form factor, magnetization and relaxation factor). This crude approximation is made possible after observing that linewidth variation with temperature observed for F1 and F2 is similar even though they have different mean diameters and Zn concentration (Fig. 1). Therefore, we have simplified our approach by taking only one value for the relaxation parameter inside a given magnetic fluid. With this approximation one gets a simple relation between the resonance fields $H_{r_0}^{\perp}$ and $H_{r_0}^{\|}$ which are theoretically calculated without relaxation and $H_r^{\perp}$ and $H_r^{\|}$, the corresponding resonance fields, calculated with relaxation. The latter are associated to the experimental values of resonance fields: $\delta H_r = H_r - H_{r_0} = -\frac{3}{4}(\Delta H_{pp})^2\gamma/\omega_{rf}$. where ω_{rf} is the frequency of the microwave field, $\gamma = g_{eff}\mu_B/\hbar$ is the gyromagnetic factor, μ_B the Bohr magneton, g_{eff} the effective Lande factor, and ΔH_{pp} the peak-to-peak linewidth. Using the classical relations:

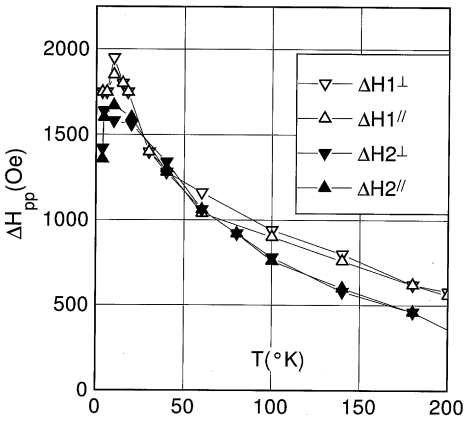

Fig. 1. ΔH_{pp} as a function of temperature for ferrofluids F1 ($\Delta H^{\|}1, \Delta H^{\perp}1$) and F2 ($\Delta H^{\|}2, \Delta H^{\perp}2$).

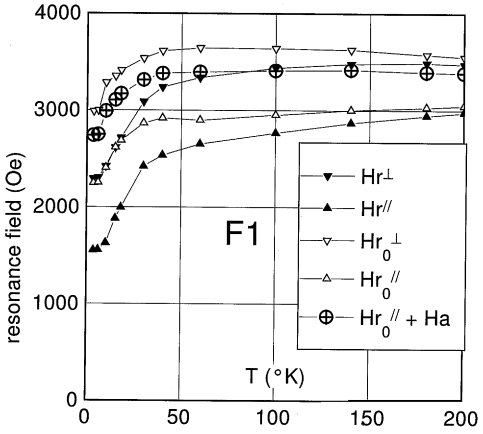

Fig. 2. Resonance field as a function of temperature for ferrofluid F1 ($x_1 = 0.5$): experimental values (H_r), relaxation corrected values (H_{r_0}) and $H_{eff} = H_{r_0} + H_a$.

$\omega_{rf}/\gamma = H_{r_0}^{\|} + H_a = [H_{r_0}^{\perp}(H_{r_0}^{\perp} - H_a)]^{1/2}$ [3] one gets, with a good approximation, the *uniaxial* anisotropy field H_a:

$$H_a = 2/3(H_{r_0}^{\perp} - H_{r_0}^{\|}). \quad (1)$$

The variations of $H_r^{\| - \perp}$, $H_{r_0}^{\| - \perp}$ and H_a with temperature are shown in Figs. 2 and 3 for F1 and F2. We have also represented the quantity $H_{r_0}^{\|} + H_a$, theoretically equal to ω_{rf}/γ thus changing slightly with T as g_{eff}^{-1}.This is experimentally observed for the temperature range $T > 40$ K $= T_f$.

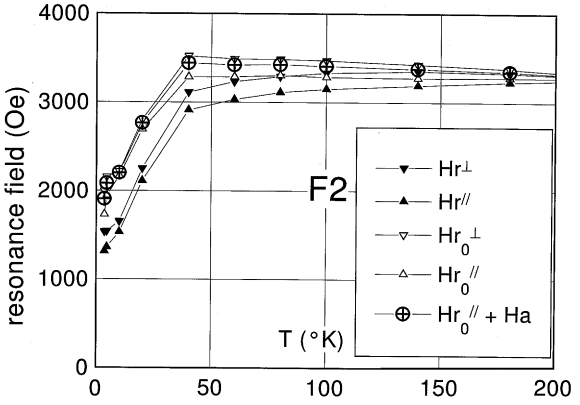

Fig. 3. Resonance field as a function of temperature for ferrofluid F2 ($x_2 = 0.63$): experimental values (H_r), relaxation corrected values (H_{r_0}) and $H_{eff} = H_{r_0} + H_a$.

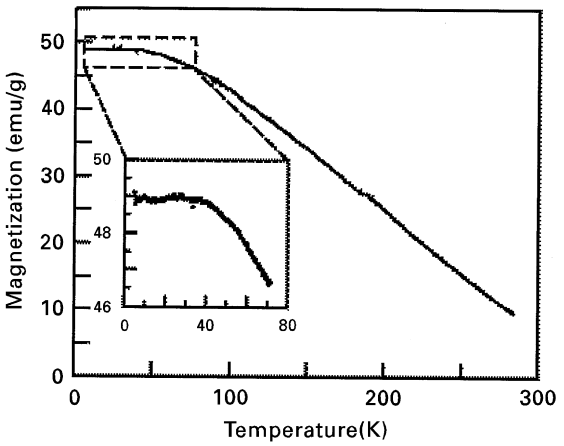

Fig. 4. Temperature dependency of magnetization of powder P2 ($x_2 = 0.63$) with an insert of the range 0–75 K. Supplied magnetic field is 3 kOe.

For $T < 40$ K, we have also observed, independently from relaxation effects, a shift of the resonance field. This shift does not depend on applied H_{DC} field orientations. We have related this observation to the appearance of an *unidirectional* anisotropy field H_u, directed along the applied H_{DC} field.

We obtain the value of H_u by the relation:

$$H_u = (\omega_{rf}/\gamma)^* - (H_{r_0}^{\parallel} + H_a), \quad (2)$$

where $(\omega_{rf}/\gamma)^*$ is the practically constant value of $H_{r_0}^{\parallel} + H_a$ for $T > T_f$ (Figs. 2 and 3).

H_u is also detected indirectly in the low magnetic field spectrum which is determined by the magnetization processes preceding the recording. For example, if the magnetic fluid sample has been magnetized in a given direction, then studied by RFM with H_{DC} field increasing from zero in a different direction, H_u is destroyed in the initial direction and reconstructed in the new H_{DC} direction. Therefore, the effective field $H_{DC} + H_a + H_u$ has a nonlinear variation with H_{DC} and we have observed a deformation of the low field spectrum.

Temperature measurements of magnetization were made on particles P2 either as powder or as magnetic fluid (F2) in an applied magnetic field of 3000 Oe. We have observed a steady increase in magnetization as temperature decreases in the range of 290–40 K, and a plateau for $T < 40$ K (Fig. 4). At room temperature, measurements on powder P2 show no saturation of magnetization up to 160 KOe.

3. Discussion

For $T > 40$ K, H_a (Fig. 5) increases slowly with decreasing temperature for the two ferrofluids with a magnitude larger for F1 than F2. This is in agreement with a linear dependence of H_a on the magnetization if we assume that H_a derives from a demagnetization field. The form factor of 1.1–1.2 as observed by electronic microscopy for our particles reinforces our hypothesis. In addition to that, the Zn substitution rate for P1 and P2 particles correspond to a P1 magnetization higher than that of P2 according to the well-known magnetization curve of bulk $Mn_{1-x}Zn_xFe_2O_4$ [4].

In this temperature range, the linewidth increases rapidly and reaches a maximum near T_f. We assume the increasing influence of a local random magnetic field induced by the magnetic inhomogeneity.

For $T < 40$ K, the unidirectional anisotropy field H_u obtained by Eq. (2) is observed directly in Figs. 2 and 3 as the shift of $H_{r_0}^{\parallel} + H_a$. It appears exactly in the same temperature range as the plateau of the static field-cooled susceptibility (Fig. 4).

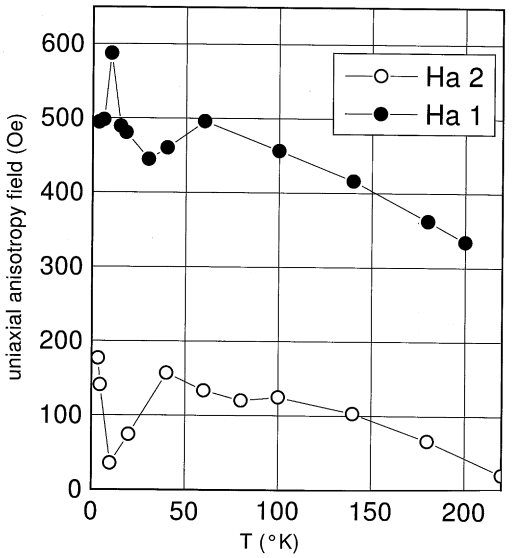

Fig. 5. Uniaxial anisotropy field $H_a = \frac{2}{3}(H_{ro}^{\perp} - H_{ro}^{\parallel})$ as a function of temperature: H_{a1} for ferrofluid F1 ($x_1 = 0.5$) and H_{a2} for ferrofluid F2 ($x_2 = 0.63$).

These features are typical [5–7] of a transition from a disorder ferromagnetic phase to a spin-glass phase (i.e. reentrant behavior), with a freezing temperature $T_f \cong 40$ K. The random Zn substitution of magnetic ions on A and B sites induced a deterioration of magnetic interactions inside and between the magnetic sub-lattices, and so favors spin-glass state at low temperature. This was earlier studied by Villain [8] who depicted the conditions in which spin-glass behavior and disordered ferromagnetism appear in magnetic spinels. As observed in Figs. 2 and 3 H_u magnitude is notably larger for F1 than for F2, this is related to the higher Zn concentration for F2 ($x_2 = 0.62$) than for F1 ($x_1 = 0.50$), as we observed previously.

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