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Magnetic resonance of zinc- and copper-ferrite ionic magnetic fluids: temperature effects

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Abstract

Magnetic resonance was used to investigate ionic magnetic fluids based on $ZnFe_2O_4$ and $CuFe_2O_4$ nanoparticles. Temperature and angular variation measurements were performed with field-frozen samples, using an X-band spectrometer. The resonance line shape analysis indicates the presence of four components, irrespective of the temperature and sample orientation. Intermediate values of the anisotropy field were associated to dimers, while low and high values of the anisotropy field were associated to large- and small-sized monomers, respectively. The temperature dependence of the resonance field associated to each resonance line allowed quantitative investigation of the surface anisotropy component. Positive as well as negative surface anisotropy components, as obtained from the temperature dependence of the resonance field, are reported.

Keywords: Resonance—magnetic; Magnetic fluids; Ferrites; Anisotropy—fine particles

Over the last two decades, magnetic resonance (MR) has been proved to be a powerful technique to investigate magnetic nanoparticles immersed in a non-magnetic matrix [1]. It has been successfully employed in the study of ionic [2] and surfacted [3] magnetic fluids (MFs). MR experiments have also been used to investigate surface charge–discharge processes [4], particle–particle interaction [5], anisotropy field [6], and exchange field [7]. Despite many experimental evidences of resonance line structure all the MF investigations performed to date have used the linewidth and the resonance field obtained from the envelope resonance line [2–7]. As a consequence, important details such as dimer formation [8] and exchange mode manifestation [9] have been neglected. In this study, the analysis of the resonance field will be focused on several components of the magnetic resonance spectra.

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The resonance frequency (ω_R) of a nanomagnetic center in the presence of an effective magnetic field (H_{EFF}) is given by $\omega_R = \gamma H_{EFF}$, where γ is the gyromagnetic ratio. The effective magnetic field is a result of the external sweeping field (H_E), the demagnetization field (H_D), the exchange field (H_X), and the effective anisotropy field (H_{EK}). In other words, $H_{EFF} = H_E + H_D + H_X + H_{EK}$. Following Callen and Callen H_{EK} can be expanded in terms of spherical harmonics

$$H_{EK} = \sum_l \sum_m H_{kl} P_l^m(\cos\alpha)\exp(im\varphi),$$

where $P_l^m(\cos\alpha)$ are Legendre polynomials, and H_{kl} are effective anisotropy field coefficients [10]. The exchange field is given by $H_X = 4cv^2/M_S D^\beta$, where c is the exchange constant, v are eigenvalues of the differential equation involving the spherical Bessel functions $dj_n(v)/dv = 0$, M_S is the saturation magnetization, D is the nanoparticle diameter, and $\beta \leqslant 2$ [11,12]. In the case of spherical ($m = 0$) and uniaxial ($l = 2$) nanoparticles the angular dependence of the magnetic resonance field reads

$$H_R = (\omega_R/\gamma - H_D - 4cv^2/M_S D^\beta) - H_{EK}, \quad (1)$$

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where $H_{EK} = (H_{k2}/2)(3\cos^2\alpha - 1)$. As long as the cavity frequency and temperature remain unchanged the resonance field in Eq. (1) may be written as a combination of an angular-independent (H_{R1}) plus an angular-dependent term (H_{R2}), namely, $H_R = H_{R1}(D) + H_{R2}(D,\alpha)$. At this point, it is important to stress the usefulness of Eq. (1), once it allows determination of the anisotropy field and surface anisotropy associated to the nanomagnetic particles.

Symbols in Fig. 1 show the typical angular dependence of the resonance field associated to each one of the single resonance lines of the copper-ferrite-based MF sample, while the solid lines represent the best fit of the experimental data according to Eq. (1). The best numerical fit of the envelope resonance line was achieved with four resonance lines, for all the temperatures ($100 < T < 260$ K) and sample orientation values ($0 \leqslant \alpha \leqslant 190°$). The MR spectra of the zinc-ferrite-based MF sample also show four components, with similar angular dependence of the resonance field. The identification of each one of the single resonance lines resulting from the deconvolution procedure is a quite difficult task. Nevertheless, the analysis based on angular variation measurements of the field-frozen MF samples seems to provide the best strategy to identify the resonance line with a particular magnetic entity. 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 would result from the fanning and coherent coupling of medium-sized nanoparticles, as recently discussed elsewhere [8]. The best fit of the angular variation data (250 K) give the H_{R1} values of 3139.7, 3006.0, 3435.1, and 3427.1 gauss for the resonance lines A, B, C, and D, respectively ($ZnFe_2O_4$ MF sample). Likewise, the H_{R1} values of 2431.2, 3188.7, 3529.1, and 3703.6 g associated to the resonance lines A, B, C, and D, respectively, were obtained for the $CuFe_2O_4$ MF sample. At 250 K, the H_{k2} values of 45.9, 26.6, 34.1, and 79.6 g were obtained for the resonance lines A, B, C, and D, respectively ($ZnFe_2O_4$ MF sample). At 250 K, the H_{k2} values of 81.4, 146.6, 178.3, and 144.9 g were obtained for the resonance lines A, B, C, and D, respectively ($CuFe_2O_4$ MF sample). Note that the H_{k2} parameter associated to the B and C resonance lines are basically the same, indicating resonance lines associated to magnetic entities which are very similar to each other. However, the H_{k2} parameter associated to A and D resonance lines are quite different from one another and from the H_{k2} parameters associated to B and C resonance lines. This is a strong indication that A and D resonance lines are related to magnetic entities which are quite different. It is claimed here that differences in the H_{k2} parameter should result from differences in size of distinct magnetic entities (large- and small-sized), due to the surface contribution ($H_S = 6h_S/D$), where h_S would be a complicated function

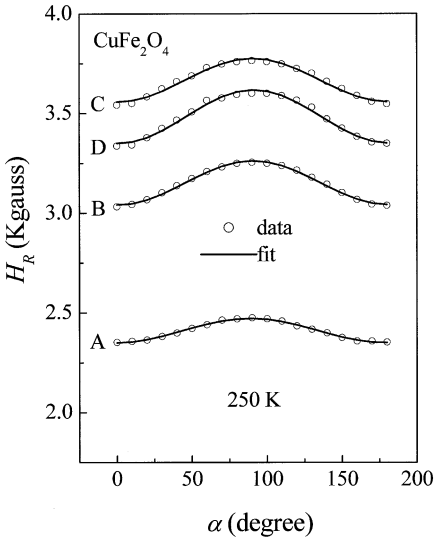

Fig. 1. Symbols represent the angular dependence of the resonance field (copper ferrite at 250 K) associated to the resonance lines (A, B, C, and D) while the solid lines represent the best fit of the experimental data according to Eq. (1).

of the temperature [13]. In fact, a more detailed analysis of the angular variation data indicates that the B and C resonance lines would be associated to similar mid-sized magnetic entities, differing only in the exchange mode values (different v values).

Symbols in Fig. 2 represent typical temperature dependence of the resonance field of the zinc-ferrite-based MF sample associated to each one of the single resonance lines (A, B, C, and D). Eq. (1) is used once again to explain the temperature dependence of the resonance field. Inspection of Eq. (1) reveals that the temperature dependence of the resonance field is mainly associated to the last term on the right-hand side (H_{k2}), through its dependence upon the effective magnetocrystalline anisotropy density (K_{EFF}). K_{EFF} has both bulk (K_B) and surface (K_S) components, i.e., $K_{EFF} = K_B + K_S$ [12]. The effective anisotropy field in spherical spinel ferrite nanoparticles is given by $H_{k2} = 2K_{EFF}/M_S$. Inspection of the temperature dependence of the resonance field for the two MF samples show a linear relationship between H_R and T. In other words, the effective magnetic anisotropy would be empirically represented by $K_{EFF} = K_0 + k_{EFF}T$, where K_0 is a constant and k_{EFF} is expressed in units of erg/cm^3 K. Straight lines in Fig. 2 represent the best fit of the data using the empirical relation $H_R = b + aT$, where $b = (\omega_R/\gamma - H_D - H_X - 2K_0/M_S)$ and $a = 2k_{EFF}/M_S$. The best fit of H_R versus T in the case of the $ZnFe_2O_4$ MF sample gives the k_{EFF} values of 1.54, 2.68, -0.36, and -0.57 erg/cm^3 K for the resonance lines A, B, C, and D, respectively.

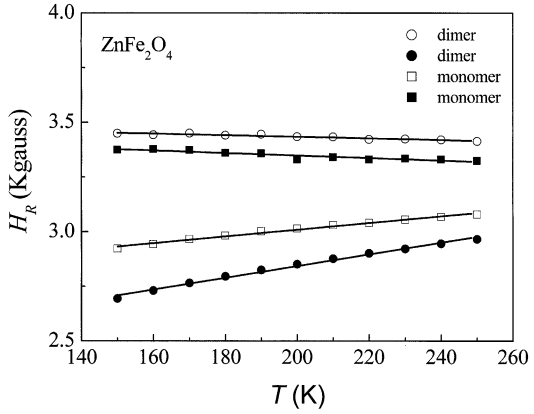

Fig. 2. Symbols represent the temperature dependence of the resonance field (zinc ferrite at $\alpha = 0$) associated to the resonance lines (A, B, C, and D) while the solid lines represent the best fit of the experimental data according to the linear function $H_R = b + aT$.

Likewise, the k_{EFF} values of 2.13, 1.15, 0.20, and 0.38 erg/cm^3 K were obtained, for the resonance lines A, B, C, and D respectively, in the case of the $CuFe_2O_4$ sample.

In summary, temperature and angular variation measurements have been performed in field-frozen copper- and zinc-ferrite-based ionic MF samples, from 100 K till the melting point. Such an experimental strategy allows resonance line shape analysis to be carried out with identification of the contributing magnetic structures. The resonance lines A and D occurring at low and high resonance fields are associated to large- and small-sized spherical monomers, respectively. However, the resonance lines B and C are associated with dimers, built up from spherical mid-sized nanoparticles. The surface anisotropy component (K_S) is obtained from the temperature dependence of the resonance field associated to each resonance line. While copper-ferrite-based nanoparticles only display positive values of K_S, zinc-ferrite-based nanoparticles display positive as well as negative values of K_S. The signal associated to K_S may be due to radial or tangential orientation of the spins located on the nanoparticle surface.

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