

Use of magnetic resonance to investigate magnetic fluids for transformers application

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Magnetic resonance (MR) was used to investigate two magnetic fluid (MF) samples containing nanosized (average 3 nm in diameter) iron oxide particles suspended in insulating mineral and vegetal oils. The MR spectra were analyzed using two Lorentzian-like components. Analysis of the temperature (T) dependence of the resonance field (H_R) indicates that the lower-field (higher-field) resonance line accounts for monomers (chain-like units). The solid-liquid phase transition of the MF samples, taking place around the melting point of the insulating oil (solvent), is indicated by a cusp in the $H_R \times T$ curve, which is more pronounced for the lower-field resonance line component. This finding was associated to a higher reorientation of the monomer's magnetic moment upon melting of the MF sample.

Keywords: Transformer; magnetic fluid; magnetic resonance; nanoparticle.

Resonancia magnética (RM) fue utilizada para investigar dos muestras de fluidos magnéticos (FM) conteniendo nanopartículas (diámetro medio de 3 nm) de óxido de hierro suspendidas en un aislante mineral y aceite vegetal. El espectro de RM fue analizado usando dos componentes de forma lorentziana. El análisis de la dependencia de la temperatura (T) con el campo resonante (H_R) indica que a bajos campos (campos superiores) la línea de resonancia produce monómeros (unidades tipo cadena). En la transición de fase solida-líquido las muestras de FM próximo al punto de descongelamiento del aceite aislante (solvente), es indicado por la cúspide en la curva $H_R \times T$, que es más pronunciada para la componente de la línea de resonancia a bajos campos. Este ajuste fue asociado para la alta reorientación de los momentos magnéticos de los monómeros encima del punto de descongelamiento de las muestras de FM.

Descriptores: Transformador; fluido magnético; resonancia magnética; nanopartículas.

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1. Introduction

Over the last two decades magnetic resonance (MR) has been proved to be a powerful technique to investigate magnetic nanoparticles supported in non-magnetic templates [1]. In particular, it has been successfully employed in the study of magnetic fluid (MF) samples [2]. Development of insulating magnetic oil for use in high voltage transformers requires production of highly-stable MF samples, allowing high dilution rates in the insulating oil plus operation at elevated temperatures and under high voltages for long periods of time [3]. In this study MR has been used to investigate particle-particle interaction within clusters formed by agglomeration of individual magnetic particles while suspended in MF samples based on insulating mineral and vegetable oils. The analysis of the MR spectra in the temperature range of 115 to 360 K was performed using two resonance components, herein describing isolated nanoparticles and chain-like units.

2. Experimental

Preparation of the MF sample for application in transformers was accomplished in four-steps. In the first step magnetite nanoparticle was synthesized by co-precipitation of Fe(II) and Fe(III) ions in alkaline medium. In the second step the oxidation of the as-produced magnetite to maghemite was

performed by adding HCl aqueous solution to the black precipitate (setting the pH at 3.5). The suspension was heated at 97°C under stirring while oxygen was bubbled throughout the medium for 3 hours. The resulting suspension was centrifuged and the oxidized precipitate isolated and washed with distilled water. In the third step pure oleic acid (OA) was added under stirring to the previously-oxidized precipitate. At the end of the third step the OA-coated nanoparticles were captured in organic phase, following separation from the aqueous phase by decantation. Ethanol was used to wash the powder consisting of OA-coated nanoparticles in order to remove the excess of free oleic acid. The powder sample consisting of OA-coated nanoparticles were then dried to remove out the ethanol and used for suspension in insulating mineral and vegetable oils, producing two distinct MF samples (4 g of the OA-coated nanoparticles in 100 mL of insulating oil). The two MF samples based on insulating mineral and vegetable oils were labeled MFM and MFV, respectively. The powder sample obtained before the OA-coating step was investigated using X-ray diffraction (XRD) in order to obtain the average size of the nanoparticulated material. The average diameter obtained using the Scherrer's relation [4] was about 3 nm. The MR measurements were performed in a Bruker ESP-300 spectrometer operating in the X-band region (about 9.4 GHz). The MR measurements were performed in the temperature range of 115 to 360 K, in steps of

10 K from 115 to 285 K, and in steps of 15 K from 285 K to 360 K. The MF samples were frozen from room temperature down to about 115 K under zero-field condition. From the lower temperature end (115 K) the MR spectra were recorded by heating the samples to higher temperatures (360 K). The scans for all samples were performed in the same range of magnetic field.

Typical MR spectra shown in Fig. 1 are the first derivative of the microwave absorption signal. The visible asymmetric shapes of the MR spectra indicate the presence of different magnetic structures (isolated nanoparticles and clusters), as previously reported for MF samples based on surface-coated nanoparticles [5]. Therefore, all the MR spectra were curve fitted using two Lorentzian-shaped components, describing the resonance lines accounting for isolated nanosized particles (monomers) and clusters (chain-like structures). The dashed lines included in Fig. 1 (245 K and 360 K) show the typical Lorentzian-shaped components. Symbols in Figs. 2a and 2b show the temperature dependence of the resonance field ($H_R \times T$) of the two Lorentzian-shaped components obtained from the analysis of the mineral oil-based and vegetable oil-based MF samples, respectively. For both MF samples investigated the higher-field (lower-field) components were labeled La (Lb). Except for a small temperature window, the anomaly around 200 K (250 K) for the mineral oil-based (vegetal oil-based), the $H_R \times T$ data show a monotonic behavior with the resonance field linearly increasing as the temperature increases. For both MF samples the anomaly (cusp) observed in the $H_R \times T$ data is higher for the lower-field resonance components. Finally, the lower-field resonance components present higher slope than the higher-field resonance components. However, the slope of the $H_R \times T$ curve for the lower-field resonance components is about the same above and below the observed cusp. In contrast, the slope of the $H_R \times T$ curve for the higher-field resonance components is much lower above than below the observed cusp. The linearity observed in the $H_R \times T$ data can be explained by the approach already described in the literature [6].

3. Results

The cusp observed in the $H_R \times T$ curves (see Fig. 2) is associated to the melting of the insulating oil as the temperature increases from below the oils' melting point. Note that the melting point of vegetable oils occurs at higher temperatures (in the range of 225 to 275 K) in comparison to the melting point of mineral oils (transition temperature in the range of 165 to 225 K). To account for the temperature dependence of the resonance field ($H_R \times T$) the resonance frequency (ω_R), *i.e.* the Larmor precession frequency of the nanoparticle's magnetic moment in the presence of an effective magnetic field (H_{EFF}), is written as,

$$\omega_R = \gamma H_{EFF}, \quad (1)$$

where γ is the gyromagnetic ratio. The H_{EFF} may be well describe as 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,

$$H_{EFF} = H_E + H_D + H_X + H_{EK}. \quad (2)$$

At the resonance condition, H_E matches the resonance field, which is describe by [6],

$$H_R = \omega_R/\gamma - H_D - H_X - H_{EK}. \quad (3)$$

The effective anisotropy field in spherical nanosized spinel ferrite particles is given by

$$H_{EK} = 2K_{EFF}/M_S, \quad (4)$$

where M_S is the saturation magnetization. The effective magnetocrystalline anisotropy (K_{EFF}) has both bulk (K_B) and surface (K_S) components, *i.e.* [7],

$$K_{EFF} = K_B + K_S. \quad (5)$$

The surface component is related to the surface-to-volume ratio by $K_S = (6/D)k_S$, where D is the nanoparticle diameter and k_S is the surface anisotropy [8]. The effective magnetic anisotropy is empirically represented by,

$$K_{EFF} = K_0 + k_{EFF}T, \quad (6)$$

where K_0 is a constant and k_{EFF} is a size-dependent coefficient which is related to the K_{EFF} temperature change rate (expressed in units of erg/cm³K). Inspection of the points in $H_R \times T$ curves (see data on Fig. 2) shows a linear behavior both below and above the freezing temperature of the carriers.

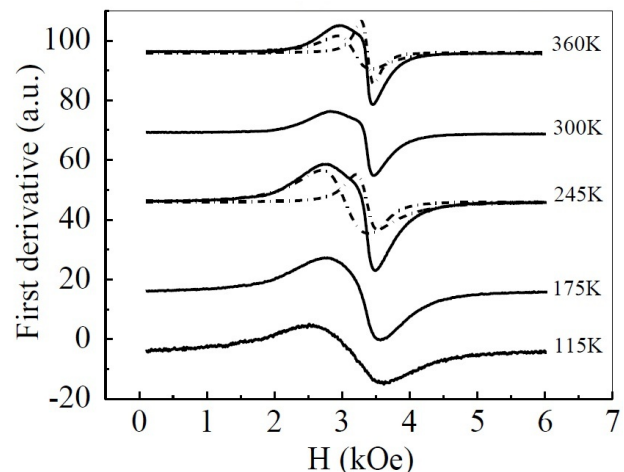


FIGURE 1. Typical MR spectra of sample MFM containing nanosized iron oxide particles (5.31×10^{16} particle/cm³) at various temperatures.

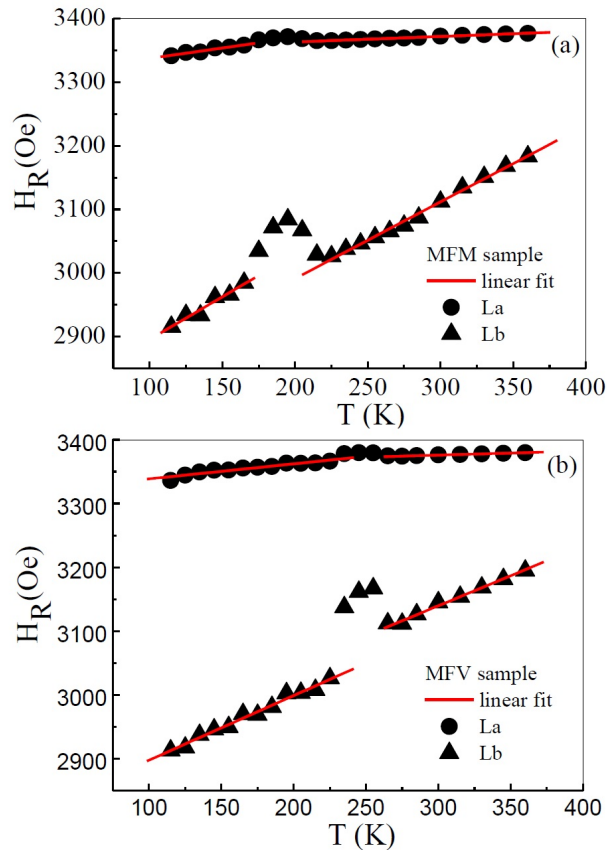


FIGURE 2. Temperature dependence of the resonance field of the two MR components associated to samples (a) MFM and (b) MFV.

The empirical relation,

$$H_R = A + BT, \quad (7)$$

where $A = (\omega_R/\gamma - H_D - H_X - 2K_0/M_S)$ is the intercept constant and $B = 2k_{EFF}/M_S$ is the slope [6], was used to fit the $H_R \times T$ data shown in Figs. 2a and 2b. Comparing the empirical relation $K_{EFF} = K_0 + k_{EFF}T$ with $K_{EFF} = K_B + K_S$, one identifies K_0 with K_B and $k_{EFF}T$ with $(6/D)k_S$. At this point we argue that k_{EFF} is directly proportional to $6/D$, meaning that the B parameter scales with $(1/D)$. Straight lines in Figs. 2a and 2b represent the best fit of the $H_R \times T$ data using the empirical relation $H_R = A + BT$. Table I collects the parameters A and B obtained from the fitting of the $H_R \times T$ data for both MF samples, above and below the cusp around 200 K (250 K) for the mineral oil-based (vegetal oil-based).

4. Discussion

Analysis of the parameters collected on Table I reveal that the B ratios (lower-field over higher-field) in the frozen condition are about 4.2 and 4.4 for samples MFM and MFV, respectively. This finding is a strong support to the picture that in both MF samples the lower-field resonance line component accounts for monomers (Lb) whereas the higher-field

TABLE I. Parameters obtained from the linear fitting of the $H_R \times T$ data using the following equation: $H_R = A + BT$.

Sample	Parameter	Below melting point		Above melting point	
		La	Lb	La	Lb
MFM	A (Oe)	3304.8	2761.4	3345.8	2750.1
	B (Oe/K)	0.32	1.34	0.08	1.20
MFV	A (Oe)	3315.0	2796.0	3356.7	2856.7
	B (Oe/K)	0.23	1.01	0.06	0.94

resonance line component accounts for tetramers (La). It is equally interesting to quote that for both MF samples the B parameter associated to the lower-field component, above and below the melting point, are very much close together, indicating that monomer units are preserved at the solvent solid-liquid phase transition. However, for both MF samples a change on the B parameter associated to the higher-field component, above and below the melting point, is observed, indicating that tetramer units are not preserved at the solvent solid-liquid phase transition. Actually, the values of the B parameter quoted on Table I for both MF samples indicate that the average size of the magnetic units responsible for the higher-field magnetic resonance component is about four times larger in the liquid phase than in the solid phase. The findings regarding the change on the magnetic unit size at the solid-liquid phase transition help shine some light on the intensity of the observed cusp. While frozen under zero-field condition monomers may present the spatial magnetic moment (and easy-axis) orientation randomly distributed. In contrast, while frozen under zero-field condition tetramers may present local order due to the stronger interaction among neighboring units. Therefore, at the solid-liquid transition under the effect of the applied sweeping field (H_E), reorientation of single magnetic units is much more pronounced than reorientation of long chain-like magnetic units. Strong interaction among short chain-like neighboring magnetic units could be the key point to built long chain-like magnetic units at the solid-liquid transition. Indeed, values of the A parameters presented on Table I are consistent with the picture presented above and related to single (monomers) and chain-like magnetic units. A higher sweeping field (H_E) is required for the resonance condition associated to chain-like magnetic units in order to compensate for the built in demagnetizing field (H_D). In contrast, spherically-shaped monomers present no demagnetizing field, thus requiring lower values of sweeping field (H_E) to meet the resonance condition.

5. Conclusions

In conclusion, this study shows that magnetic resonance measurements of magnetic fluid samples based on mineral and vegetable oils successfully help to build a picture of the samples internal structure with nanosized particles organized as single and chain-like units. This approach is very much

promising in analyzing the samples internal structure at temperatures around 400 K, which is the typical temperature for operation of electrical transformers. While using the technology of insulating magnetic oil the heat exchange efficiency between the transformers inner and the outer parts is influenced by the magnetic oil's internal structure. Therefore, besides the basic interest while understanding the particle-particle interaction of suspended nanosized magnetic particles magnetic resonance measurements of insulating mag-

netic oils in the temperature range of transformer's operation is of great help while optimizing the insulating magnetic oil technology.

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