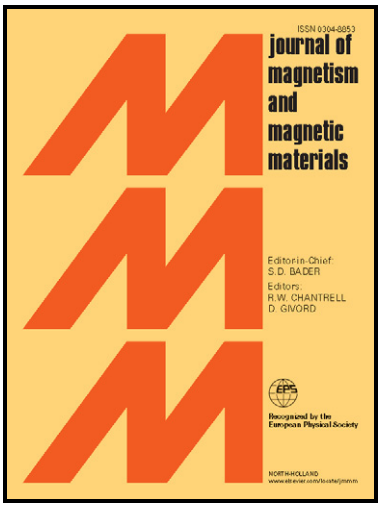


www.elsevier.com/locate/jmmm

The resonance decay function method in the determination of the pre-factor of the néel relaxation time of single-domain nanoparticles

P.C. Fannin, C.N. Marin, C. Couper

PII: S0304-8853(10)00788-2
DOI: doi:10.1016/j.jmmm.2010.11.014
Reference: MAGMA 56570

To appear in: *Journal of Magnetism and Magnetic Materials*

Cite this article as: P.C. Fannin, C.N. Marin and C. Couper, The resonance decay function method in the determination of the pre-factor of the néel relaxation time of single-domain nanoparticles, *Journal of Magnetism and Magnetic Materials*, doi:10.1016/j.jmmm.2010.11.014

The Resonance Decay Function Method in the Determination of the Pre-factor of the Néel Relaxation Time of Single-domain Nanoparticles

P. C. Fannin[a,1]*, C. N. Marin[b], C. Couper[a]

[a]Department of Electronic and Electrical Engineering, Trinity College, Dublin 2, Ireland

[b]West University of Timisoara, Faculty of Physics, B-dul V. Parvan, no.4, 300223, Timisoara, Romania

Abstract

In its simple form, the relaxation time of the Néel relaxation process of the magnetic moment of single-domain particles is given by $\tau_N = \tau_{0N} exp(\sigma)$, σ being the ratio of the anisotropy energy to thermal energy. The pre-factor, τ_{0N} , is normally given a value of 10^{-9} s, but values ranging from 10^{-8} to 10^{-12} *s* have been reported in literature. Here, by means of the field and frequency dependence of the complex magnetic susceptibility, $\chi(\omega,H)= \chi'(\omega,H)-i\ \chi''(\omega,H)$, of a magnetic fluid sample, in the MHz – GHz range, in conjunction with the determination of the sample decay function, $b(t)$, the pre-factor τ_{0N} is determined. $b(t)$ is readily obtained through the inverse Fourier transformation relationship which exists between $b(t)$ and $\chi''(\omega)$.

PACS: 47.65.Cb; 75.40.Gb; 76.50.+g

Keywords: magnetic fluids; dynamic susceptibility; ferromagnetic resonance

* Corresponding author. Tel.: +35318961860; fax: +35316772442.
E-mail address: pfannin@tcd.ie

1. Introduction

Magnetic fluids are stable colloidal systems consisting of single-domain magnetic particles covered by a surfactant in order to prevent particle agglomeration and dispersed in a carrier liquid [1]. The particles have radii usually ranging from approximately 2-15 nm and they are considered to be in a state of uniform magnetization with a magnetic moment, $m = M_S v$, where M_S denotes the saturation magnetization and v is the magnetic volume of the particle.

The dynamics of the magnetic moment, $\vec{m}$, of a single-domain magnetic particle is described by the Landau-Lifshitz equation [2]:

$$\frac{d\vec{m}}{dt} = -\gamma\left(\vec{m}\times\vec{H}_t\right) - \frac{\alpha\gamma}{m}\left[\vec{m}\times\left(\vec{m}\times\vec{H}_t\right)\right] \tag{1}$$

where $\vec{H}_t$ is the total field, including the polarizing field, $\vec{H}$, the anisotropy field, $\vec{H}_A$ and the dipolar interparticle interaction field, $\vec{H}_D$, $\gamma = \mu_0 g \frac{e}{2m_e}$ is the gyromagnetic ratio, μ_0 is the free space permeability, g is the spectroscopic splitting factor of the material of the particle, e = 1.6·10^{-19} C is the charge of the electron and m_e = 9.1·10^{-31} kg is the mass of the electron.

The first term on the right side of Eq.(1) represents the free precession of the magnetic moment, $\vec{m}$ around $\vec{H}_t$ with the Larmor frequency $\omega_0 = \gamma H_t$, while the second term describes the decay of this precession. This second term must have the dimension of magnetic moment over time, as the derivative $\frac{d\vec{m}}{dt}$ and therefore the ratio $\frac{1}{\alpha\gamma H_t}$ must have the dimension of time. This time, $\tau_{0,H} = \frac{1}{\alpha\gamma H_t}$ is known as the precessional decay time. In zero polarizing fields, for particles with uniaxial anisotropy, the precessional decay time can be written as,

$$\tau_0 = \frac{M_S}{2\alpha\gamma K} \tag{2}$$

Here, M_S is expressed in Tesla (M_S in *A/m* multiplied by μ_0) and K is the effective uniaxial anisotropy constant, which includes the effects of shape, magneto-crystalline field and dipolar interparticle interaction field.

The frequency dependant susceptibility, $\chi(\omega,H)$, of such an assembly of single domain magnetic particles can be described in terms of its parallel, $\chi_{||}(\omega,H)$, and perpendicular, $\chi_{\perp}(\omega,H)$, components with respect to the total field, $\vec{H}_t$, by the equation [3]:

$$\chi(\omega,H) = \frac{1}{3}\left[\chi_{||}(\omega,H) + 2\chi_{\perp}(\omega,H)\right] \tag{3}$$

In strong H_t with respect to k_BT (k_B is the Boltzmann's constant and T is the temperature), the perpendicular susceptibility, $\chi_{\perp}(\omega,H)$ can be expressed in its Landau-Lifshitz form [3, 4]:

$$\frac{\chi_{\perp}(\omega,H) - \chi_{\perp\infty}(H)}{\chi_{\perp}(0,H) - \chi_{\perp\infty}(H)} = \frac{1 + i\omega\tau_{0,H} + \omega_0^2\tau_{0,H}^2}{(\omega_o^2 - \omega^2)\tau_{0,H}^2 + 1 + 2i\omega\tau_{0,H}} \tag{4}$$

The parallel or longitudinal susceptibility component, $\chi_{||}(\omega,H)$ can be described by the Debye equation [3,5], with

$$\chi_{||}(\omega,H) = \chi_{||\infty}(H) + \frac{\chi_{||}(0,H)}{1 + i\omega\tau_{||}} \tag{5}$$

where $\chi_{||}(0,H)$ is the parallel susceptibility at frequencies much lower than the frequency, $f_{||max}$ at which the imaginary component of $\chi''(\omega,H)$ is a maximum, $\chi_{||\infty}(H)$ is the parallel susceptibility at very high frequencies (but below resonance) and $\tau_{||}$ is the parallel relaxation time. $\tau_{||}$ is related to the frequency, $f_{||max}$, by the expression, $f_{||max} = 1/(2\pi\tau_{||})$.

There are two relaxation times which influence the magnetic relaxation in magnetic fluids: i) the Brownian relaxation time, τ_B, which is determined by the rotation of particles in the carrier liquid [3], and ii) the Néel relaxation time, τ_N, correlated to the rotation of the magnetic moment of particles, by overcoming the energy barrier within the particles [3].

For the Néel relaxation time, in zero polarizing fields, the following approximate expressions are valid [6, 7]:

$$\tau_N = \begin{cases} \tau_0 \sigma & for \quad \sigma << 1 \\ \tau_0 \sigma^{-1/2} \exp(\sigma) & for \quad \sigma \geq 2 \end{cases} \tag{6}$$

where $\sigma = \dfrac{Kv}{k_B T}$ is the ratio of anisotropy energy to thermal energy.

For single-domain magnetic particles with uniaxial anisotropy, a general expression used to describe the Néel relaxation time is the well-known Arrhenius like formula [1]:

$$\tau_N = \tau_{0N} \exp(\sigma) \tag{7}$$

J. L. Dormann and co-workers [8-12], as well as other researchers [13-15] have experimentally determined the pre-factor, τ_{0N} of Eq. (7), for different single-domain particle systems and found values ranging from 10^{-8} to 10^{-13} s. Their experimental method was based on the thermal variation of the Néel relaxation time (in fact on the dependence of the logarithm of the Néel relaxation time, $log(\tau_N)$, on the inverse of the blocking temperature, $1/T_B$).

The objective of this work is to present a different technique for the determination of the pre-factor, τ_{0N}, of single-domain magnetic particles in magnetic fluids, but the method can be used in all single-domain magnetic particles systems.

2. Theoretical considerations on the experimental method

The perpendicular or transverse susceptibility, $\chi_\perp(\omega,H)$, can have a resonant character, whereby precession of the magnetic moment occurs about the total field, $\vec{H}_t$. In equilibrium, the magnetic moment, $\vec{m}$, would be directed along $\vec{H}_t$ if it were not for thermal fluctuations. The extent of this disturbance depends on σ. In the case of a small disturbance, the angular resonant frequency, ω_0 is given by $\omega_0 = \gamma H_t$.

If a microwave frequency field is applied perpendicular to $\vec{H}_t$, the motion of the magnetic moment has a typical resonant character with the existence of a resonance

phenomenon being indicated by a transition in the value of $\chi_{\perp}'(\omega,H)$ from a +ve to a -ve quantity at a frequency, f_{res}.

The decay or after-effect function, *b(t)*, represents the decay of magnetization after the sudden removal of an external polarizing magnetic field, and $\chi''(\omega,H)$ is related to *b(t)* by the expression [16],

$$b(t) = 2\,\mathrm{Re}\left\{F^{-1}\left[\frac{\chi''(\omega,H)}{\omega}\right]\right\} \tag{8}$$

were F^{-1} denotes the inverse Fourier transform.

B. K. P. Scaife [17] has shown that the after-effect function of the Landau-Lifshitz equation has the form:

$$b_{LL}(t) = b_{LL}(0)\exp\left(-\frac{t}{\tau_{0,H}}\right)\cos\omega_0 t \tag{9}$$

If the microwave field is not perpendicular to $\vec{H}_t$, its perpendicular component determines the resonance phenomenon and its parallel component is responsible for the relaxation phenomenon. The Debye after-effect function is given by the expression [17].

$$b_D(t) = \left[\chi_{\parallel}(0,H) - \chi_{\parallel\infty}(H)\right]\exp\left(-\frac{t}{\tau_{\parallel}}\right) \tag{10}$$

Generally speaking, the overall complex magnetic susceptibility is a superposition of Landau-Lifshitz and Debye terms and the corresponding after effect function is a superposition of Landau-Lifshitz and Debye after effect functions (Eq.(9) and Eq.(10)).

For magnetic fluids subjected to a polarizing field, *H*, the static parallel susceptibility decreases with the field [18] and therefore in strong polarizing fields the Debye after-effect function vanishes. Consequently, in strong polarizing fields, the overall after-effect function reduces to the Landau-Lifshitz after-effect function $b_{LL}(t)$. If the area under $b_{LL}(t)$ is denoted by *B(H)*, then using Eq.(9), it follows that in strong polarizing fields [4],

$$\frac{B(H)}{b_{LL}(0,H)} = \frac{\tau_{0,H}}{1+\omega_0^2\tau_{0,H}^2} \tag{11}$$

Bearing in mind that in strong polarizing fields $\omega_0=2\pi f_{res}$ [19], by knowing the normalized area under the after-effect function, $B(H)/b_{LL}(0,H)$, experimental values of $\tau_{0,H}$ can be determined from Eq.(11).

The theoretical expression of the precessional decay time is given by Eq. (12), where H_A is the effective anisotropy field (including the magnetocrystalline, shape and dipolar interparticle interaction effects).

$$\tau_{0,H} = \frac{1}{\alpha\gamma(H+H_A)} \tag{12}$$

In Ref. [20] is shown that for values of the polarizing field larger than the anisotropy field ($H>H_A$), the polarizing field dependence of f_{res} can be written in the form of Eq.(13).

$$f_{res} = \frac{\gamma}{2\pi}(H+H_A) \tag{13}$$

Since Eq.(13) is the equation of a straight line, from the plot of f_{res} against H, the experimental value of the anisotropy field, H_A is obtained. Now, making use of the experimental value of H_A in Eq.(12) and then fitting it to the experimental dependence $\tau_{0,H}(H)$, the value $\tau_0 = \tau_{0,H}(0)$ can be determined.

For single-domain particles with uniaxial anisotropy, the ratio $\sigma = \frac{Kv}{k_BT}$ of the anisotropy energy to the thermal energy may be written as:

$$\sigma = \frac{vH_AM_S}{2k_BT} \tag{14}$$

With τ_0 and σ determined as above, the pre-factor, $\tau_{0N} = \tau_0\sigma^{-1/2}$ can be determined.

3. Experimental results and discussions

The sample investigated was a kerosene-based magnetic fluid with magnetite particles of mean diameter 10 nm, having a saturation magnetization of 0.09 Tesla.

Measurements of frequency and polarizing field dependence of the complex magnetic susceptibility, $\chi(\omega, H) = \chi'(\omega, H) - i\,\chi''(\omega, H)$, were made by means of the coaxial transmission line technique [21, 22], using a Hewlett Packard (HP) 50Ω coaxial line incorporating a coaxial cell, in conjunction with an HP 8753C network analyzer. The biasing field, H, was varied between 0 and 100 kA/m.

In order to increase the accuracy of the Fourier transform (Eq.(8)), by increasing the number of the experimental points, the data for the sample was fitted with theoretical dependencies as in Ref. [23]. The corresponding fit to the χ' and χ'' are shown in Figs. 1 and 2 respectively. These show how the resonant frequency, f_{res}, varies from 1.76 GHz to 5.25 GHz, whilst the frequency of the maximum of the χ'' component, f_{max}, varies from 1.23 GH to 4.7 GHz, over the range of the polarizing field, H. It should be noted that the fit extends to 20 GHz in comparison to the 6 GHz upper frequency of the measured data.

Fig.1

Fig.2

Fig.3 shows a plot of f_{res} against H. In order to satisfy that the condition $H>H_A$ (condition for which the linear dependence (13) is applicable [20]), only the experimental values of f_{res} corresponding to values of the polarizing field larger than 50 kA/m were used. By use of Eq.(13), a value of H_A = 50.94 kA/m is determined for the sample.

Fig.3

From the fit data of Fig.2 the after-effect functions were computed by means of equation (8) and the results are shown in Fig.4. From the figure it is clearly seen how the function changes from an exponential type decay to an oscillatory one over the polarizing field range. In fact the final form of the after effect function becomes similar to that of the Landau Lifshitz form (Eq.(9)).

Fig.4

By computing the area under the plots of Fig.4 and making use of the experimental values of ω_{res} ($\cong \omega_0$) in Eq.(11), the solutions of $\tau_{0,H}$ of Eq.(11) were determined and the results are shown in Fig 5.

Fig.5

As can be observed from Fig.5, for the analyzed sample, Eq.(11) has real solutions for polarizing fields larger than approximately 10 kA/m. Furthermore, Eq.(11) is a quadratic equation and has two solutions, say, τ_1 and τ_2 (see Fig.5). The correct values of the precessional decay time, $\tau_{0,H}$, can be determined by testing the values of τ_1 and τ_2 with the theoretical equation (12), bearing in mind α cannot be larger than one and using the experimental value of the anisotropy field. Performing the same test for all solutions of τ_1 and τ_2, we determine that the correct solutions of Eq.(11) are those of τ_1. One also notes from Fig. 5 that τ_1 falls with increasing H, for values larger than approximately 60kA/m. This behavior is in agreement with Eq.(12), which results from the Landau-Lifshitz equation. As long as the after-effect function is a superposition of the Debye and Landau-Lifshitz after-effect functions one can assert that up to approximately 60 kA/m the relaxation process contributes to the overall after-effect function whilst in polarizing fields larger than 60 kA/m, the resonance process becomes more significant than the relaxation process. One also notes that the effective anisotropy field is 50.94 kA/m (see Fig.3), and therefore one can assert that the resonance behaviour of the sample becomes of the Landau-Lifshitz type in polarizing fields larger than the effective anisotropy field.

The theoretical dependence of $\tau_{0,H}$ (Eq.(12)) was fitted to the experimental dependence $\tau_1(H)$ of Fig.5, using the experimental value of the effective anisotropy field, H_A=50.94 kA/m. The fit parameter was the product $\alpha\gamma = 6.84 \cdot 10^4\ mA^{-1}s^{-1}$.

From Eq.(12) we note that the precessional decay time in zero polarizing field, $\tau_0 = \frac{Ms}{2\alpha\gamma K}$, is simply the value of equation (12) at H=0. By fitting the data to equation (12) and extrapolating the fit of Fig.5 back to H=0, a value of $\tau_0 = \tau_{0,H}(0)$ is obtained. For the investigated sample, τ_0 was found to be $2.87 \cdot 10^{-10}$ s.

Using the measured value of the effective anisotropy field, and assuming uniaxial anisotropy, the effective anisotropy constant is given by $K = H_A M_S/2$. Taking into account the spontaneous magnetization of magnetite, M_S = 0.6 Tesla [24], one obtains the effective anisotropy constant, $K=1.5 \cdot 10^4 J/m^3$. One can observe that the experimental value of the anisotropy constant is larger than the value of the anisotropy constant measured on a magnetite crystal, $K_1 = 1.1 \cdot 10^4\ J/m^3$ [25]. This difference is due to the fact that the anisotropy constant experimental determined here is an effective one, including the magnetocrystalline, shape and interparticle interaction effects. In Ref. [26] is experimentally shown that the effective anisotropy constant depends on the particle concentration (the larger the particle concentration, the larger the value of the effective anisotropy constant), a result which is in agreement with the theoretical models of Shtrikman-Wohlfarth [27] and Dormann-Bessais-Fiorani [9, 10].

With this value of K and the average diameter of the particles, d=10 nm, one gets the ratio of the anisotropy energy to the thermal energy, σ = 1.93. The prefactor $\tau_{0N} = \tau_0 \sigma^{-1/2}$ of the Néel relaxation time results in $\tau_{0,N}=2.06 \cdot 10^{-10}$ s. This value is in agreement with the results presented in Refs. [8] and [14] for magnetic fluids with magnetite particles, results that have been obtained from the dependence of the logarithm of the Néel relaxation time on the inverse of the blocking temperature, $1/T_B$; a different technique to that used here.

4. Conclusions

A new method for the determination of the value of the Neel pre-factor, τ_{0N}, has been presented. The method centers on the measurement of the field and frequency dependent magnetic complex susceptibility, $\chi(\omega, H) = \chi'(\omega, H) - i\,\chi''(\omega, H)$ and the relationship which exists between the χ'' component and the decay function, $b(t)$, from which the precessional decay time of the Landau-Lifshitz equations can be determined. It is shown that by extrapolating the plot of the field dependence of the precessional decay time, $\tau_{0,H}(H)$, against H, back to zero, a value of τ_{0N} may be determined. With this value and the ratio of the anisotropy energy to the thermal energy, σ, the pre-factor, $\tau_{0N}=2.06\cdot10^{-10}$s is determined. This value of τ_{0N} determined here for a magnetic fluid with magnetic particles, is in agreement with the value of τ_{0N} reported by other researchers using a different method [8, 14], however this proposed method has the advantage of being performed at room temperature.

Acknowledgements

P.C.Fannin acknowledges ESA for part funding of this work and also M Hennessy for support given. C. N. Marin gratefully acknowledges partial financial support from CNMP grant no. 1-32155/2008.

References

[1] R. E. Rosensweig, *Ferrohydrodynamics*, Cambridge Univ. Press (1985).

[2] L. D. Landau and E. M. Lifshitz, Phys. Z. Sowjetunion, 8 (1935) 153, reprinted in *Collected Works of Landau*, Pergamon Press, London, No. 18 (1965).

[3] Yu. L. Raikher and M. I. Shliomis, Adv.Chem.Phys., *Relaxation Phenomena in Condensed Matter*, vol. 87, ch.8, (1994) 595-751.

[4] P.C. Fannin, C. N. Marin and C. Couper., *J. Magn. Magn. Mater.* 320 (2010) 1682

[5] P. Debye, *Polar Molecules*, The Chemical Catalog Company, New York, 1929.

[6] W. F. Brown Jr., Phys. Rev., 130 (1963) 1677.

[7] Yu. L. Raikher and M. I. Shliomis, *JETP*, 67 (1974) 1060.

[8] J. L. Dormann, D. Fiorani, E. Tronc, J. Magn. Magn. Mater., 202 (1999) 251.

[9] J.L. Dormann, L. Bessais, D. Fiorani, *J. Phys. C* 21 (1988) 2015.

[10] J.L. Dormann, D. Fiorani, E. Tronc, *Adv. Chem. Phys.* 98 (1997) 283.

[11] J.L. Dormann, F. D'Orazio, F. Lucari, E. Tronc, P. Prené, J.P. Jolivet, D. Fiorani, R. Cherkaoui, M. Nogue`s, *Phys. Rev. B* 53 (1996) 14291

[12] J.L. Dormann, R. Cherkaoui, L. Spinu, M. Nogués, F. Lucari, F. D'Orazio, D. Fiorani, A. Garcia, E. Tronc, J.P. Jolivet, *J. Magn. Magn. Mater.* 187 (1998) L139.

[13] M. Hayashi, M. Susa, K. Nagata, *J. Magn. Magn. Mater.* 171 (1997) 170.

[14] J. Zhang, C. Boyd, W. Luo, *Phys. Rev. Lett.* 77 (1996) 390.

[15] C. Djurberg, P. Svedlinh, P. Nordlab, M.F. Hansen, F. Bodker, S. Morup, *Phys. Rev. Lett*. 79 (1997) 5154.

[16] P.C. Fannin, *Journal of Molecular Liquids* 114, Issues 1-3, (2004) 79.

[17] B. K. P. Scaife, *Principles of dielectrics*, Clarendon Press, Oxford, 1998.

[18] P. C. Fannin, B. K. P. Scaife, S. W. Charles, *J. Phys. D: Appl.* Phys., 21 (1988) 533.

[19] P.C.Fannin, C.N.Marin, I.Mălăescu, J. Phys.: Condensed Matter 15 (2003) 4739.

[20] P. C. Fannin, C. N. Marin, V. Socoliuc, G. M. Istratuca, A. T. Giannitsis, J. Phys. D: Appl. Phys. 36 (2003) 1227.

[21] P.C. Fannin, T. Relihan, S.W. Charles, *J. Phys. D: Appl. Phys.*, 28 (1995) 2003.

[22] P.C. Fannin, C. MacOireactaigh, C. Couper, *J. Magn. Magn. Mater.*, 322 (2010) 2428.

[23] P.C. Fannin, T. Relihan, S.W. Charles, *Phys. Rev. B*, 55 (1997) 14423.

[24] E.Kneller, *Ferromagnetismus*, Springer-Verlag, Berlin, (1962)

[25] L.R. Bickford, *Phys. Rev.* 78 (1950) 449.

[26] C.N.Marin, I.Mălăescu, A.Ercuța, J.Phys.D: Appl. Phys. 34 (2001) 1466.

[27] S. Shtrikman, E.P. Wohlfarth, Phys. Lett. 85 A (1981) 457.

Figure captions

Fig.1. Plots of fit to $\chi'(\omega)$ against *f(GHz)* for the investigated sample.

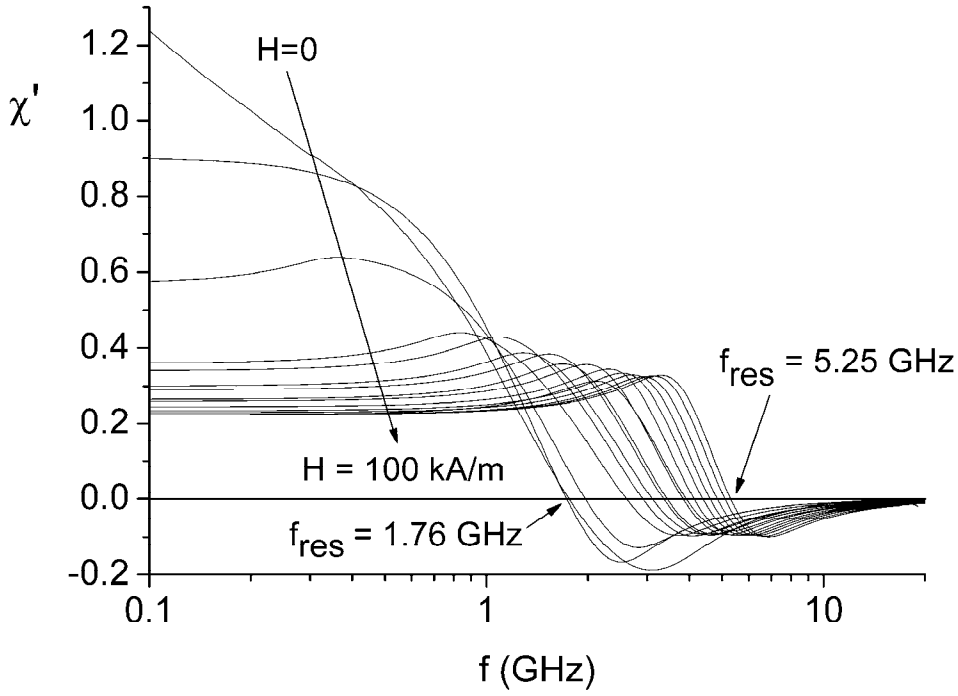


Fig.2. Plots of fit to $\chi''(\omega)$ against *f(GHz)* for the investigated sample.

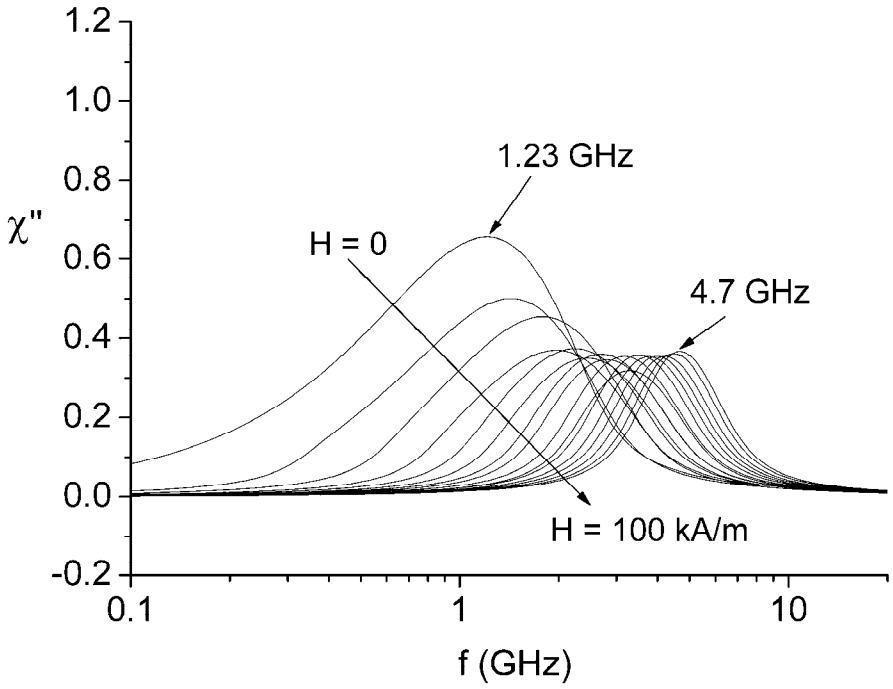


Fig.3. Plot of f_{res} against H for the investigated sample.

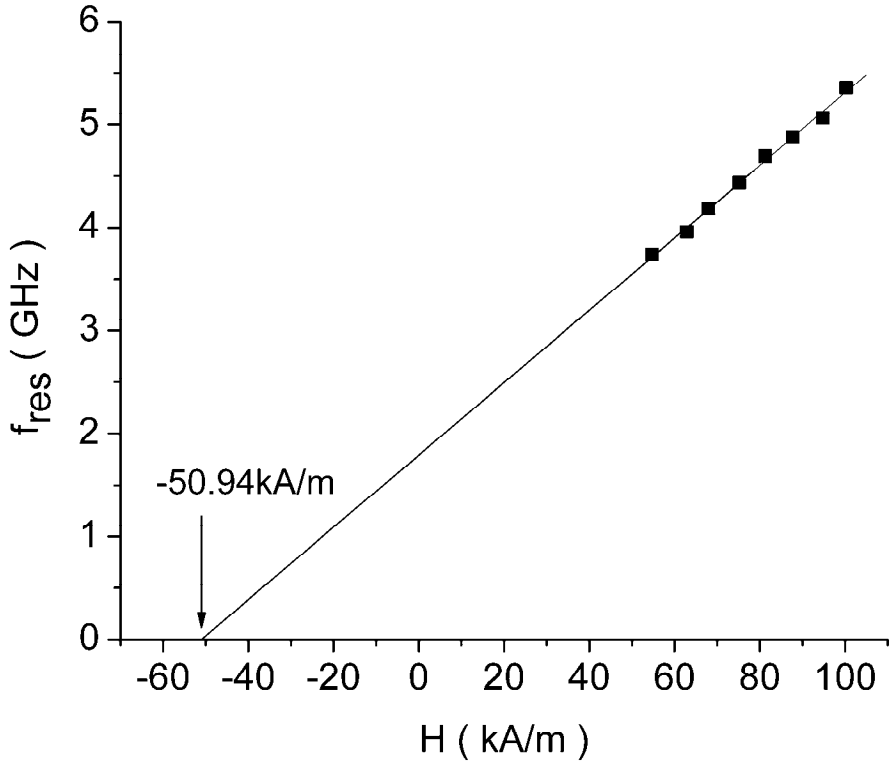


Fig.4. Plot of the normalized after effect functions against *t(s)*, for the investigated sample.

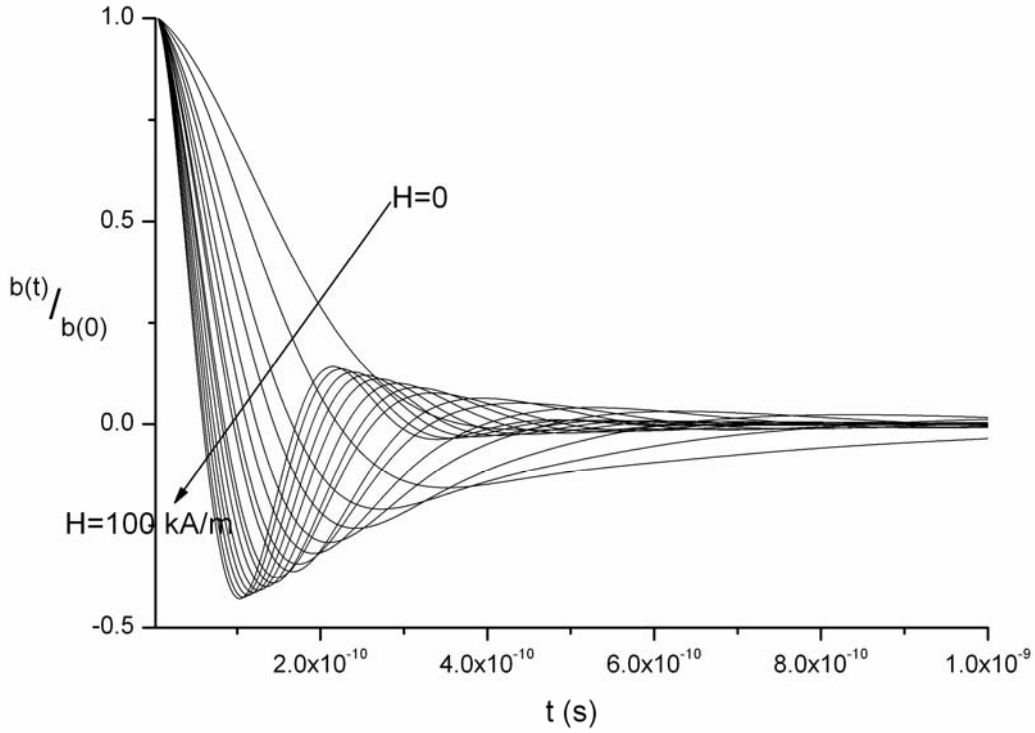
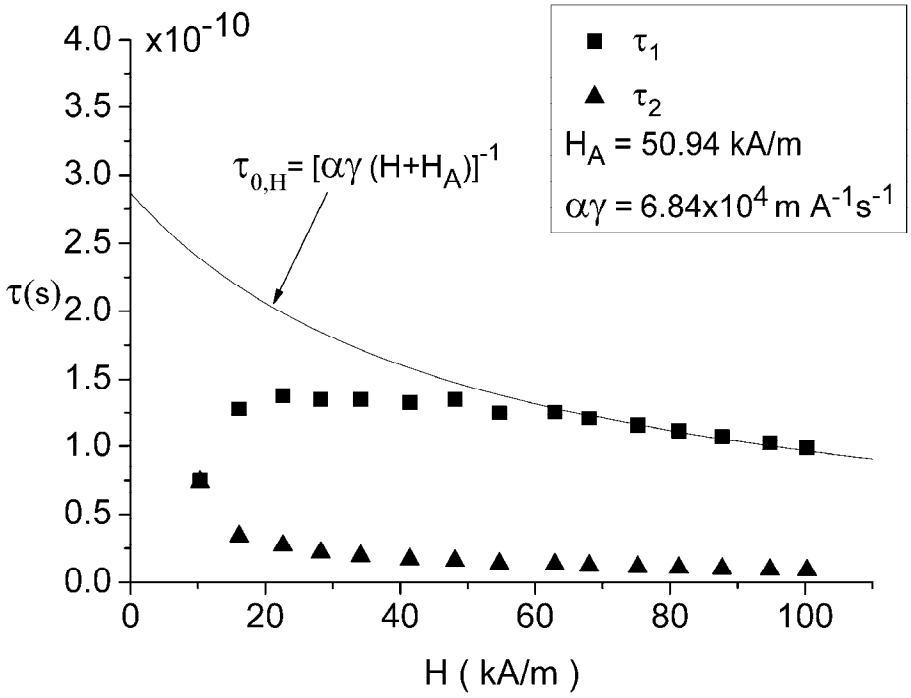


Fig.5. Plots of the solutions of Eq.(11) against *H* and of the theoretical Landau-Liftshitz expression of the decay time (full line).



Research Highlights. Paper MAGMA_56570

- Experimental technique centred on the measurement of the complex magnetic susceptibility, $\chi(\omega, H) = \chi'(\omega, H) - i\,\chi''(\omega, H)$.
- The precessional decay time of the Landau-Lifshitz equations is evaluated.
- Néel pre-factor, τ_{0N}, determined for single-domain magnetite particles of mean diameter 10 nm.
- After-effect function, b(t), obtained through the relationship which exists between $b(t)$ and $\chi''(\omega)$.