

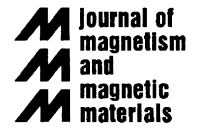


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Investigation of the complex susceptibility of magnetic beads containing maghemite nanoparticles

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Abstract

We report on frequency and field-dependent complex susceptibility, $\chi_s(\omega) = \chi'_s(\omega) - i\chi''_s(\omega)$, measurements of a magnetic colloidal system consisting of 200 nm spherical beads, containing maghemite ($\gamma\text{Fe}_2\text{O}_3$) nanoparticles. The relaxation properties of both the magnetic colloid and a free suspension of the $\gamma\text{Fe}_2\text{O}_3$ particles, are investigated over the frequency range 200 Hz–1 MHz.

Under a polarizing field H , an absorption peak is detected in the χ''_s component at frequencies f_{max} between 1.1 and 1.7 kHz. We show that this absorption peak can be attributed to the Néel relaxation of the inner maghemite nanoparticles. It is also shown that the general trend for the value of f_{max} and the amplitude of both χ'_s and χ''_s is to increase with increasing H . Furthermore, the relation between $\chi'_s(\omega)$ and $\chi''_s(\omega)$ and their dependence on frequency, $\omega/2\pi$, is investigated by means of the magnetic analogue of the Cole–Cole plot and a measure of the Cole–Cole distribution parameter α_s is determined.

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1. Introduction

Superparamagnetic colloids [1] are presently used in many fundamental and applied fields of research. For instance, the use of such colloids with beads coated with antibodies that specifically bind to specific proteins is of current interest in the area of medical diagnosis [2].

The magnetic spheres investigated here have a diameter of 200 nm and were supplied by Ademtech [3]. They are made by evaporating the solvent (octane) in emulsions of an organic ferrofluid. Emulsions are colloidal systems constituted of droplets of a liquid dispersed in another immiscible one; the droplets being stabilized by a surfactant. Once the solvent is evaporated, the solid-like spheres contain 50% volume fraction of maghemite particles of approximately 10 nm mean radius (as measured by Dynamic Light Scattering), the surfactant being oleic acid. With spheres of this diameter (200 nm) the dominant

relaxation mechanism could be due to either Brownian [4] or Néel relaxation [5]. As far as the considered spheres are composite materials, the inner component (maghemite particles) could also contribute to the relaxation. However, the maghemite particles are extremely confined inside the spheres (almost close-packed) and therefore cannot experience Brownian relaxation. The only possible contribution of the inner particles is thus their Néel relaxation.

Here we set out to determine which of these three mechanisms is dominant: Brownian relaxation of the spheres, Néel relaxation of the spheres or Néel relaxation of the inner particles.

Single domain particles have a magnetic moment, m_p , given by

$$m_p = M_s v, \quad (1)$$

where M_s denotes the saturation magnetisation and v is the magnetic volume of the particle.

The Brownian relaxation time τ_B is given by [4]

$$\tau_B = 4\pi r^3 \eta / kT, \quad (2)$$

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where r is the hydrodynamic radius of the particle, η is the dynamic viscosity of the carrier liquid, k is Boltzmann's constant and T is the absolute temperature.

In the case of the Néel relaxation mechanism, the magnetic moment may reverse direction within the particle by overcoming an energy barrier, which for uniaxial anisotropy, is given by Kv , where K is the anisotropy constant of the particle. The associated reversal or switching time τ_N was estimated by Néel to be

$$\tau_N = \tau_0 \exp(\sigma), \quad (3)$$

τ_0 being a damping time having an approximate value of 10^{-9} s [6] and $\sigma = Kv/kT$.

When a sample contains a distribution of particle sizes, both relaxation mechanisms contribute to the magnetisation. They do so with an effective relaxation time τ_{eff} [7,8], where

$$\tau_{\text{eff}} = \tau_N \tau_B / (\tau_N + \tau_B), \quad (4)$$

the mechanism with the shortest relaxation time being dominant.

2. Complex susceptibility

The frequency dependent susceptibility, $\chi(\omega)$, may be written in terms of its real and imaginary components, where

$$\chi(\omega) = \chi'(\omega) - i\chi''(\omega). \quad (5)$$

The theory developed by Debye [9] to account for the anomalous dielectric dispersion in dipolar fluids has been used [10–12] to account for the analogous case of magnetic fluids in the approximate range 10 Hz–1 MHz.

According to Debye's theory the complex susceptibility, $\chi(\omega)$ has a frequency dependence as given by

$$\chi(\omega) - \chi_\infty = (\chi_0 - \chi_\infty) / (1 + i\omega\tau_{\text{eff}}), \quad (6)$$

where

$$\chi_0 = nm^2 / 3kT\mu_0 \quad (7)$$

and

$$\tau_{\text{eff}} = 1/\omega_{\text{max}} = 1/2\pi f_{\text{max}}, \quad (8)$$

where f_{max} is the frequency at which $\chi''(\omega)$ is a maximum, n is the particle number density and χ_0 and χ_∞ indicate susceptibility values at $\omega = 0$ and at very high frequencies.

Thus by determining f_{max} , Eq. (8) enables one to obtain the mean particle or aggregate size of the sample.

For a distribution of particle sizes a distribution of relaxation times, τ , will exist so that $\chi(\omega)$ may also be expressed in terms of a distribution function, $F(\tau)$ giving

$$\chi(\omega) = \chi_\infty + (\chi_0 - \chi_\infty) \int_0^\infty F(\tau) d\tau / (1 + i\omega\tau). \quad (9)$$

$F(\tau)$ may be represented by a range of distribution functions [13] including the Cole–Cole distribution function. In the Cole–Cole [14] case where the complex susceptibility data fits a depressed circular arc, the relation

between $\chi'(\omega)$ and $\chi''(\omega)$ and their dependence on frequency, $\omega/2\pi$, can be displayed by means of the magnetic analogue of the Cole–Cole plot [15]. In the Cole–Cole case the circular arc cuts the $\chi'(\omega)$ axis at an angle of $\alpha\pi/2$; α is referred to as the Cole–Cole parameter and is a measure of the distribution of relaxation times.

The magnetic analogue of the Cole–Cole circular arc is described by

$$\chi(\omega) = \chi_\infty + (\chi_0 - \chi_\infty) / (1 + (i\omega\tau_{\text{eff}})^{1-\alpha}), \quad 0 < \alpha < 1, \quad (10)$$

which for $\alpha = 0$, reduces to that of Eq. (6).

As the measurement frequency increases beyond approximately 1 MHz, a transition from relaxation to resonance occurs.

$\chi(\omega)$, of an assembly of single domain particles can also be described in terms of its parallel, $\chi_{\parallel}(\omega)$, and perpendicular, $\chi_{\perp}(\omega)$, components, with Ref. [16]

$$\chi(\omega) = \frac{1}{3}(\chi_{\parallel}(\omega) + 2\chi_{\perp}(\omega)). \quad (11)$$

$\chi_{\perp}(\omega)$ can have a resonant character, whereby precession of the magnetic moment occurs about an easy axis (i.e. the direction of the internal field H_A).

Under equilibrium conditions, the magnetic moment, m_p , and the anisotropy field, H_A , of a particle are parallel and any deviation of the magnetic moment from the easy axis direction results in the precession of the magnetic moment about this axis. If the polar angle θ is small, the angular resonant frequency, ω_{res} , is given in Ref. [17]

$$\omega_{\text{res}} = \gamma H_A. \quad (12)$$

H_A is the internal field for a particle with uniaxial anisotropy and where the polar angle between the easy axis and the magnetic moment is small, has magnitude, $H_A = 2K/M_s$ where K is the anisotropy constant in J/m^3 .

From Eq. (12) it can be seen that the effect of applying an external polarising field, H , results in an increase in the resonant frequency ω_{res} , which can be described approximately by

$$\omega_{\text{res}} = 2\pi f_{\text{res}} = \gamma(H + \bar{H}_A), \quad (13)$$

where \bar{H}_A represents some mean value of the anisotropy field. Eq. (13) is the equation of a straight line and from a plot of f_{res} against H , the value of \bar{H}_A can be determined from the intercept of the plot with the x -axis whilst γ is determined from the slope

3. Experimental and results

Measurements were performed on two samples:

- (i) Sample 1 which consisted of the base ferrofluid, a suspension of maghemite ($\gamma\text{Fe}_2\text{O}_3$) particles of mean particle radius 10 nm in octane, with oleic acid as surfactant; the saturation magnetization was 55 emu/g and

(ii) Sample 2 which was a dilute (0.3% volume fraction) magnetic colloid of 200 nm solid-like spheres; the spheres contained the maghemite particles of Sample 1.

We first characterized Sample 1. This was done by means of low frequency, 100 Hz–0.1 MHz and high frequency, 100 MHz–6 GHz, complex magnetic susceptibility measurements. Low-frequency measurements were made to determine whether or not the sample was aggregated and this was accomplished by means of the toroidal technique [18] in conjunction with a Hewlett Packard RF Bridge 4291A.

Fig. 1 shows a plot of $\chi'(\omega)$ and $\chi''(\omega)$ against f (Hz) obtained for Sample 1. There is no evidence of the existence of an absorption peak in the $\chi''(\omega)$ profile (which could be indicative of aggregation) and thus this fluid would be considered to be a well dispersed colloid.

The higher frequency range measurements were made by the short-circuit transmission line technique [19,20]. The measurements were performed at different values of polarising field, H , over the range 0–110 kA/m. For all values of polarizing field the $\chi'(\omega)$ component went negative thereby indicating the presence of magnetic resonance for all values of H .

Fig. 2 shows a normalized plot of the dependencies against frequency of the components of complex magnetic susceptibility, at different values of polarizing field, H , obtained in the case of Sample 1. For the unpolarised case $f_{\max} = 1.15$ GHz and $f_{\text{res}} = 1.8$ GHz and over the polarizing field range f_{\max} and f_{res} increase to 5.0 and 5.2 GHz, respectively.

The field dependence of f_{res} is given by $2\pi f_{\text{res}} = \gamma(H + H_A)$ and from a plot of f_{res} against H , the effective anisotropy field, H_A , of the maghemite particles of Sample 1 was determined as being 47.8 kA/m. Using an M_s of 0.4 T the anisotropy constant, K , is determined as

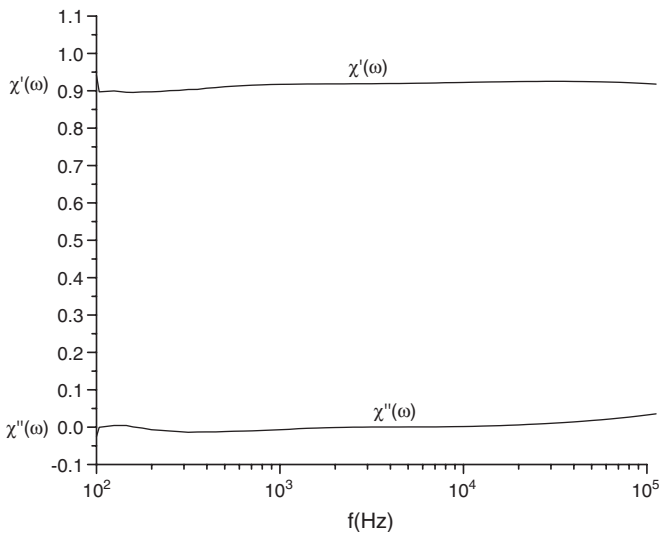


Fig. 1. Plot of $\chi'_s(\omega)$ and $\chi''_s(\omega)$ against f (Hz) over the range 10^2 – 10^5 Hz, for Sample 1.

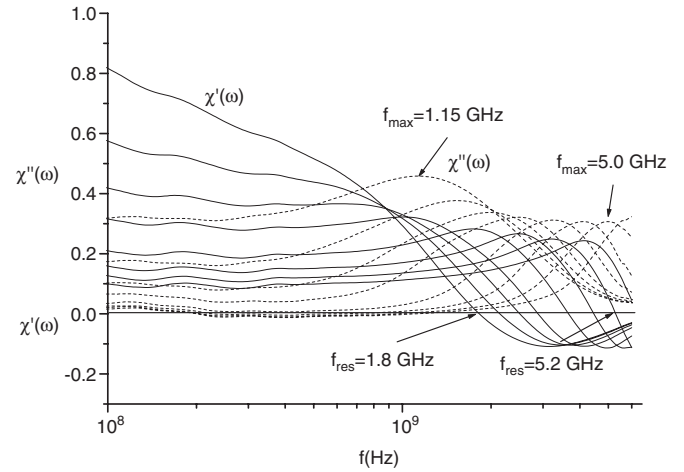


Fig. 2. Plot of $\chi'_s(\omega)$ and $\chi''_s(\omega)$ against f (Hz) over the range 10^8 – 6×10^9 Hz, for Sample 1.

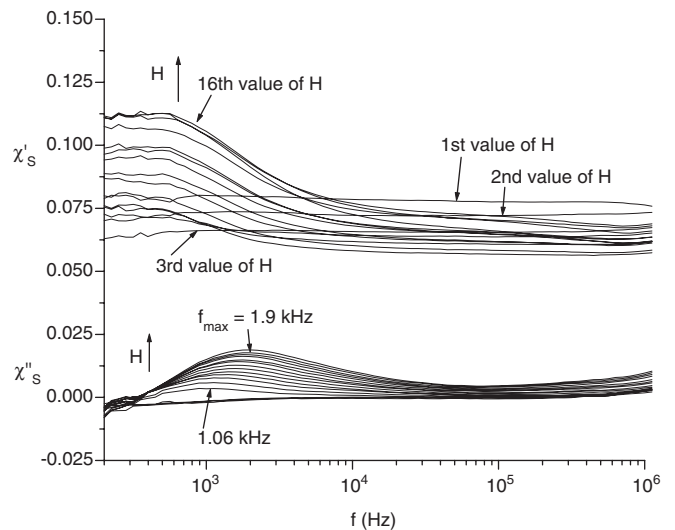


Fig. 3. Plot of $\chi'_s(\omega)$ and $\chi''_s(\omega)$ against f (Hz) for Sample 2, for 16 values of polarizing field, H .

$K = M_s H_A / 2 \approx 10^4 \text{ J/m}^3$. Furthermore, from the slope of f_{res} against H , the gyromagnetic constant, γ is found to have a value of $2.2 \times 10^5 \text{ s}^{-1} \text{ A}^{-1} \text{ m}$.

Fig. 3 shows the complex susceptibility spectra obtained for Sample 2 with the complex components being labelled as $\chi'_s(\omega)$ and $\chi''_s(\omega)$, respectively. Since the sample was a very dilute one, no useful signal was obtained below 200 Hz and for convenience, the static susceptibility, χ_{0S} was taken to be equivalent to the values of $\chi'_s(\omega)$ obtained at 400 Hz. Fig. 4 shows a plot of χ_{0S} against H , and an interesting feature of both Figs. 3 and 4 is that they clearly show an overall trend of increasing values of χ_{0S} , $\chi'_s(\omega)$ and $\chi''_s(\omega)$ with increasing H . This is in contrast to what happens in the case of magnetic fluids [14] where the equivalent

components decrease with increasing H . Furthermore an absorption peak is first detected at a frequency of $f_{\max} = 1.06$ kHz, for $H = 1.8$ kA/m, and increases to $f_{\max} = 1.9$ kHz for $H = 13.6$ kA/m.

Fig. 5 shows a Cole–Cole plot of the $\chi'_s(\omega)$ and $\chi''_s(\omega)$ components obtained for $H = 4.55$ kA/m with the corresponding value of the Cole–Cole distribution parameter, $\alpha = 0.1$. This exercise was repeated for values of H over the range 2.73–13.6 A/m and the results obtained are shown in Table 1.

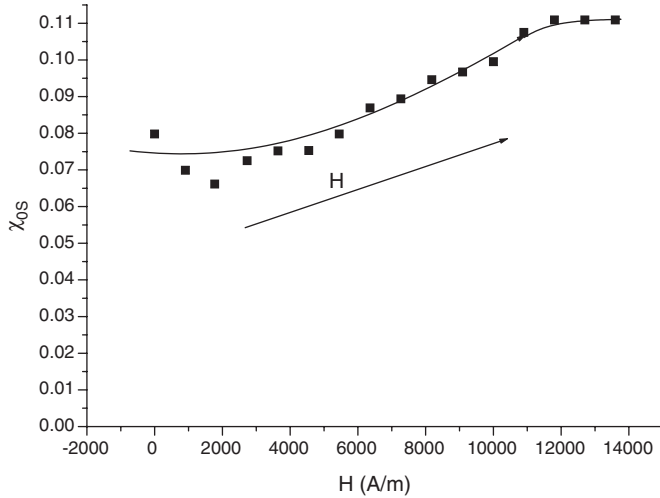


Fig. 4. Plot of χ_{0s} against H for Sample 2.

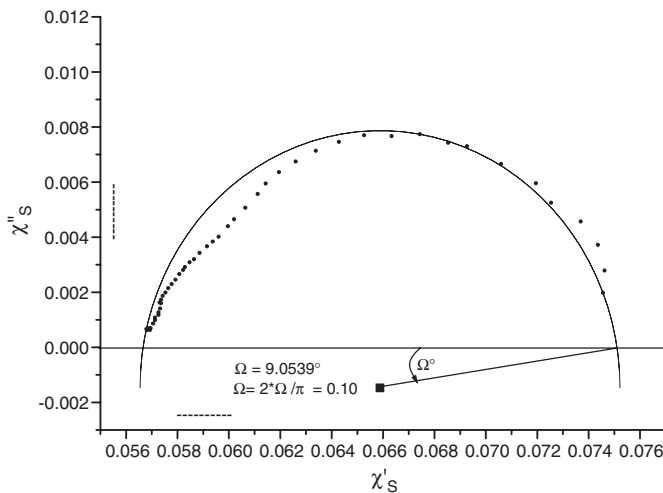


Fig. 5. Cole–Cole plot of $\chi'_s(\omega)$ against $\chi''_s(\omega)$ for $H = 4.55$ kA/m.

4. Discussion

The results present a number of interesting issues. First, we shall try to attribute the measured absorption peak to the relevant relaxation mechanism. In this perspective, let us estimate the order of magnitude of the three possible relaxation frequencies.

Experimentally, we have

$$\tau_{\text{eff}} = 1/\omega_{\max} = 1/2\pi f_{\max}.$$

In the case of Brownian relaxation (from Eq. (2)) there comes

$$1/2\pi f_{\max} = 4\pi\eta r^3/kT,$$

giving,

$$f_{\max} = kT/8\pi^2 r^3 \eta.$$

So, if we assume negligible change in viscosity η the increase in f_{\max} over the polarising field range, corresponds to a decrease in the effective hydrodynamic radius, r , of the spheres.

In the case of the magnetic spheres in a water based carrier, using a radius of 100 nm, at room temperature the Brownian relaxation time is given by

$$\begin{aligned} \tau_B &= 4\pi\eta r^3/kT \\ &= 4\pi \times 10^{-27} \times 10^6 \times 10^{-3}/4 \times 10^{-21} \\ &\approx 3 \times 10^{-3} \text{ s}, \end{aligned}$$

resulting in $f_{\max} = 1/6\pi \times 10^{-3} \approx 50$ Hz. This frequency is well outside the frequency range where the loss-peaks are detected.

In the case of Néel relaxation (from Eq. (3))

$$\tau_N = \tau_0 \exp(\sigma) \text{ with } \tau_0 \approx 10^{-9} \text{ s.}$$

Thus for spheres of 100 nm radius, with $K \approx 10^4$ J/m³ (as determined from our high frequency measurements), we get a value of $\sigma \approx 1 \times 10^4$ which corresponds to an almost infinite relaxation time that is to say to an undetectable (almost zero) frequency.

However, for a 10 nm particle, with $K \approx 10^4$ J/m³, we get a value of $\sigma = 10.5$ and $\tau_N = 3.6 \times 10^{-5}$ s. The corresponding $f_{\max} = 1/(2\pi\tau_N) \approx 4$ kHz, which is in line with the observed loss-peaks (between 1 and 2 kHz). Thus from the above calculations of the Néel and Brownian relaxation times it appears that the loss-peaks detected have their origins in the Néel relaxation of the inner maghemite particles. To conclusively confirm this fact, the susceptibility measurements were repeated with the viscosity of the carrier being increased 1000 times (by changing the carrier from water to glycerine). The result of this

Table 1

H (kA/m)	2.73	3.64	4.55	5.45	6.36	7.27	8.18	9.09	10	10.9	11.8	12.7	13.6
α	0.1	0.11	0.1	0.1	0.11	0.14	0.13	0.13	0.14	0.09	0.10	0.14	0.14

exercise showed that the frequency, f_{\max} , of the loss peaks were unchanged. Since, from Eq. (2), τ_B is directly proportional to the viscosity, η , and from Eq. (3) τ_N is independent of η , this result thus confirms that Néel relaxation of the inner particles is responsible for the loss-peaks.

The second issue raised by the results is why the complex components, $\chi'_s(\omega)$ and $\chi''_s(\omega)$ increase with increasing polarising field.

From Eq. (6), (neglecting χ_∞)

$$\begin{aligned}\chi(\omega) &= \chi_{0S}/(1 + i\omega\tau_{\text{eff}}) \\ &= \chi_{0S}(1/(1 + \omega^2\tau_{\text{eff}}^2) - i\omega\tau_{\text{eff}}/(1 + \omega^2\tau_{\text{eff}}^2)).\end{aligned}\quad (14)$$

So both $\chi'_s(\omega)$ and $\chi''_s(\omega)$ are directly proportional to χ_{0S} .

Now, since $\chi_{0S} = nm_{\text{ps}}^2/3kT\mu_0$, all parameters are fixed except for m_{ps} , the effective magnetic moment of the spheres. Thus an increase in m_{ps} could be due to the fact that the individual spheres and magnetic moments in the spheres are becoming more aligned with increasing H . So from Eq. (14) both $\chi'_s(\omega)$ and $\chi''_s(\omega)$ should increase with increasing H , as they indeed do.

It is of interest to mention that a factor which may influence the variation in $\chi'_s(\omega)$ and $\chi''_s(\omega)$ with H , is the customary diminution of $\chi(\omega)$ due to the saturation of the magnetization and this may be a contributing factor, for example, in the flattening of the χ_{0S} against H profile at higher fields.

We also note that (from Eq. (1)) $m_p = M_s v$; M_s is fixed and so only the effective magnetic volume, v , can increase, resulting in m_{ps} increasing, as stated. Of course, the actual volume of material within the spheres does not change but a change in the distribution of relaxation times of particles within the spheres may arise under the influence of the polarising field, H . The Cole–Cole plot is an established method for investigating this effect and for this purpose, data corresponding to ten values of polarising field was

fitted to Cole–Cole plots and a value of the Cole–Cole distribution parameter, α , determined in each case. Table 1 shows the results obtained and it clearly shows that the value of α increases slightly with increasing H .

Fig. 5 shows the Cole–Cole plot obtained for the case of $H = 4.55$ kA/m, where α was found to be 0.14. This value of α was inserted in Eq. (10) and a fit made to the complex components, $\chi'_s(\omega)$ against $\chi''_s(\omega)$, obtained for $H = 4.55$ kA/m. It is clear that the fit is a good one thereby confirming the value of α obtained. Fig. 6 shows the data and its fit which prove to be quite similar and testify to the accuracy of the value of α determined by means of the Cole–Cole plot.

5. Conclusion

In this paper, for the first time, measurements of the frequency dependent, complex susceptibility, $\chi_s(\omega) = \chi'_s(\omega) - i\chi''_s(\omega)$, over the frequency range 200 Hz–1 MHz, of a magnetic colloid consisting of spherical beads of 200 nm diameter, containing maghemite ($\gamma\text{Fe}_2\text{O}_3$) nanoparticles, have been presented. The relaxation properties of the colloid are investigated and it is demonstrated that the absorption peak of the $\chi''_s(\omega)$ component is due to Néel relaxation of the inner maghemite particles.

It is also shown that, unlike in the case of ferrofluids, the general trend is for the amplitude of the static susceptibility, χ_{0S} , to increase with increasing polarizing field, H .

Finally, the $\chi'_s(\omega)$ and $\chi''_s(\omega)$ data is analysed by means of the Cole–Cole plot and a measure of Cole–Cole distribution parameter, α_s , determined.

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References

- [1] F. Montagne, O. Mondain-Monval, C.H. Pichot, H. Mozzanega, A. Elaissari, J. Magn. Mater. 250 (2002) 302.
- [2] J. Baudry, E. Bertrand, N. Lequeux, J. Bibette, J. Phys. Cond. Matt. 16 (2004) 469.
- [3] www.ademtech.com.
- [4] W.F. Brown, J. Appl. Phys. 34 (1963) 1319.
- [5] L. Néel, Ann. Géophys. 5 (1949) 99.
- [6] E. Kneller, E.P. Wohlfarth, J. Appl. Phys. 37 (1966) 4816.
- [7] M.I. Shliomis, Sov. Phys. Usp. 17 (1974) 53.
- [8] M.I. Shliomis, Yu.L. Raikher, IEEE Trans. Magn. Mag. 16 (1980) 237.
- [9] P. Debye, Polar Molecules, The Chemical Catalog Company, New York, 1929.
- [10] M.M. Maiorov, Magnetohydrodynamics (cover-to-cover translation of Magnitnaia Hidrodinamika) 2 (1979) 21, 135.
- [11] P.C. Fannin, B.K.P. Scaife, S.W. Charles, J. Magn. Mater. 72 (1988) 95.
- [12] P.C. Fannin, J. Mol. Liq. 69 (1996) 39.
- [13] P.C. Fannin, Acta Phys. Polon. A 37 (2000) 3, 591.

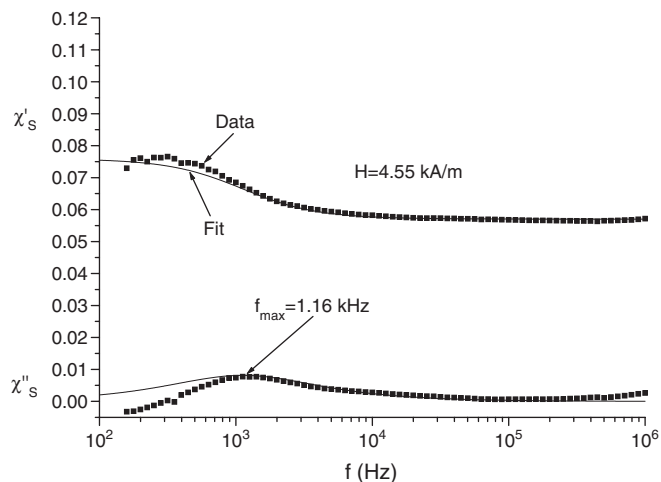


Fig. 6. Plot of data (Sample 2) obtained for $H = 4.55$ kA/m and corresponding fit obtained using Eq. (10) with $\alpha = 0.1$.

- [14] K.S. Cole, R.H. Cole, *J. Chem. Phys.* 9 (1941) 341.
- [15] P.C. Fannin, A.T. Giannitsis, *J. Mol. Liq.* 114 (2004) 8.
- [16] Y.L. Raikher, M.I. Shliomis, *Sov. Phys. JETP* 40 (1975) 526.
- [17] M.I. Shliomis, Yu.L. Raikher, *IEEE Trans. Magn. Mag.* 16 (1980) 237.
- [18] P.C. Fannin, B.K.P. Scaife, S.W. Charles, *J. Phys. E Sci. Instrum.* 19 (1986) 238.
- [19] S. Roberts, A.R. von Hippel, *J. Appl. Phys.* 17 (1946) 610.
- [20] P.C. Fannin, T. Relihan, S.W. Charles, *J. Phys. D Appl. Phys.* 28 (1995) 10, (2003).