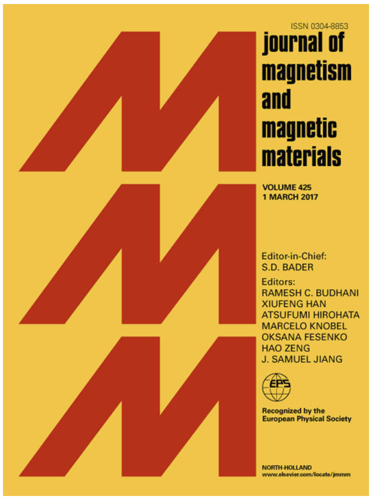

Research articles

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# Alternating current magnetic susceptibility of ferronematics: the case of high concentration of magnetic nanoparticles

Katarína Zakutanská[a], Natália Tomašovičová[a,*], Nándor Éber[b], Tibor Tóth-Katona[b], Jozef Kováč[a], Veronika Lacková[a], Jan Jadżyn[c], Peter Kopčanský[a]

[a]Institute of Experimental Physics, Slovak Academy of Sciences, Košice, Slovakia
[b]Institute for Solid State Physics and Optics, Wigner Research Centre for Physics, Hungarian Academy of Sciences, Budapest, Hungary
[c]Institute of Molecular Physics, Polish Academy of Sciences, M. Smoluchowskiego 17, 60-179 Poznań, Poland

## Abstract

The dynamic magnetic susceptibility of ferronematics (nematic liquid crystals doped with magnetic nanoparticles) has been measured for high concentrations of nanoparticles. For a given composition of the ferronematic (the same nanoparticles, and the same liquid crystal matrix) we have found the optimal volume concentration of the magnetic particles, for which the largest relative enhancement of the dynamic magnetic susceptibility is obtained upon the application of a bias magnetic field in the isotropic phase.

*Keywords:* ferronematics, magnetic susceptibility, phase transitions, magnetic nanoparticles

## 1. Introduction

Colloidal suspensions of magnetic particles (MPs) in nematic liquid crystals (LCs), known as ferronematics (FNs), have gained interest since they were invented in 1970 [1]. In comparison with neat LCs, ferronematics are highly sensitive to magnetic field [1, 2]. Their susceptibility can be several orders of magnitude higher than the susceptibility of a neat LC [3]. Even a small amount of MPs can significantly modify the properties of LCs, and besides the increased sensitivity to magnetic field, FNs show plenty of interesting optical [4], magneto-optical [5], electro-optical [6], dielectric [5, 6] or structural [7, 8, 9] characteristics.

Although, until now most of the studies were devoted to the static magnetic features of FNs, there are theoretical papers focused on magnetodynamic properties [10, 11, 12, 13]. Unfortunately, however, large amount of theoretical papers is not supported by experimental results. Recently, the dynamic susceptibility of ferronematics has been studied experimentally [14, 15]. First, we observed in an LC doped with spherical magnetic nanoparticles an enhancement $\Delta\chi'$ of the real part of the *ac* magnetic susceptibility $\chi'$ after applying a low *dc* bias field (a few Oe), which returns to its original value suddenly (and irreversibly) when the isotropic to nematic phase transition occurs [14]. Here $\Delta\chi'$ is the magnitude of the magnetic susceptibility change in the vicinity of the isotropic-to-nematic phase transition temperature. The enhancement has been found dependent on the magnitude of the *dc* bias field, however, it saturated already above 10 Oe, showing an enhancement in $\chi'$ of about 10% on the relative scale. The effect has been explained phenomenologically by the elastic energy- and defect-mediated aggregation of MPs in the nematic phase, and by the magnetic-field-assisted disaggregation in the isotropic phase [14].

More recently, an FN with the same constituents, but with a doubled concentration of the nanoparticles was investigated [15]. The increased concentration of MPs has significantly raised the value of the *dc* bias magnetic field at which the enhancement of $\chi'$ saturates (to above 500 Oe), however, the achievable maximal relative enhancement $\Delta\chi'/\chi'$ has remained roughly the same ($\approx$ 10%) as that for the lower concentration of MPs. These studies have shown, that this effect, which might be used for sensing low magnetic fields, can be significantly altered by modifying the composition, specifically, the volume concentration of magnetic nanoparticles.

The aim of the present work is to find an optimal volume concentration of magnetic particles to obtain a FN with high sensitivity to low magnetic fields, i.e., to obtain the largest relative enhancement $\Delta\chi'/\chi'$ as a response to the *dc* bias magnetic fields in the widest possible range (without saturation of $\chi'$).

## 2. Materials and Methods

The prepared samples were based on the calamitic thermotropic LC n-hexylcyanobiphenyl (6CB) [16, 17]. This LC matrix was doped with spherical MPs purchased from Ocean NanoTech (as in our previous works [14, 15]). The mean diameter of the $Fe_3O_4$ magnetic particles was $d = 20$ nm. The particles were coated with oleic acid and dissolved in chloroform. The suspension was admixed to the liquid crystal, and the solvent was let to evaporate. Ferronematic samples with two volume concentrations of nanoparticles, namely $\phi_1$=5×$10^{-4}$ and $\phi_2$=$10^{-3}$ were prepared.

For magnetic measurements the sample was filled into cylindrical capsules of 2.5 mm in diameter and 6.5 mm in length.

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[*] Corresponding author.
*Email address:* `nhudak@saske.sk` (Natália Tomašovičová)

The magnetic properties were measured with a SQUID magnetometer (Quantum Design MPMS 5XL) in a magnetic field directed along the cylindrical axis of the capsules.

The phase transition temperatures of the samples were determined by independent capacitance measurements in a capacitor made of ITO-coated glass electrodes (AWAT). The capacitor with the electrode area of approximately 5 mm×5 mm was placed into a regulated thermostat system; the temperature was stabilized with the accuracy of 0.05 °C. The distance between the electrodes (sample thickness) was $D$ = 5 μm. The capacitance was measured at the frequency of 1 kHz by a high precision capacitance bridge Andeen Hagerling. The samples were first heated to the isotropic phase; then the measurement was done in cooling at the rate of 1 K/min. The phase transition temperatures from the isotropic to the nematic phase were found at 301.3 K, 297.9 K and at 293.5 K for the neat 6CB, the FN with $\phi_1$=5×10$^{-4}$ and the FN with $\phi_2$=10$^{-3}$, respectively.

## 3. Results and Discussion

In our previous works [14, 15] the *ac* susceptibility of the ferronematics doped with these, 20 nm MPs have already been examined in two volume concentrations, 10$^{-4}$ and 2×10$^{-4}$. It has been shown that the higher volume concentration of MPs raises the value of the *dc* bias magnetic field, at which the enhancement of $\chi'$ saturates, by about two orders of magnitude in comparison with the case of the lower volume concentration of MPs. To examine how a further increment of the volume concentration of MPs influences the magnetic susceptibility of FNs against the biasing magnetic field, new ferronematics with higher volume concentrations ($\phi_1$=5×10$^{-4}$ and $\phi_2$=10$^{-3}$) of the same magnetic particles were studied. The main results of these investigations are shown in Figs. 1 and 2 for $\phi_1$=5×10$^{-4}$ and $\phi_2$=10$^{-3}$, respectively.

The *ac* magnetic susceptibility was measured in an *ac* magnetic field of 2 Oe, applied at the frequency of 10 Hz. We note here that the frequency dispersion properties of the dynamic magnetic susceptibility has already been investigated [14], and the change in the ac magnetic susceptibility was found independent of the frequency in the range from 1 Hz to 650 Hz. After exposing the samples to a *dc* bias magnetic field in the isotropic phase typically for 10 minutes, the same cooling-heating procedure was applied to the samples as in the previous works [14, 15]. To determine the temperature dependence of $\chi'$, the samples were first cooled down to the nematic phase in temperature steps of 1 K (with a cooling rate of 0.5 K$^{-1}$ between the steps). At each temperature, the susceptibility was determined after temperature stabilization for 3 minutes. After the cooling process, the same procedure was applied in heating to complete the cycle.

Figure 1 shows the temperature dependence of the real part $\chi'$ of the *ac* magnetic susceptibility for the FN with the volume concentration of MPs $\phi_1$=5×10$^{-4}$ in a cooling-heating cycle, after the *dc* bias magnetic field indicated in the legend was applied in the isotropic phase (at 307 K). On cooling, in the isotropic phase, $\chi'$ has a roughly constant value. When the sample is passing through the isotropic-nematic phase transition,

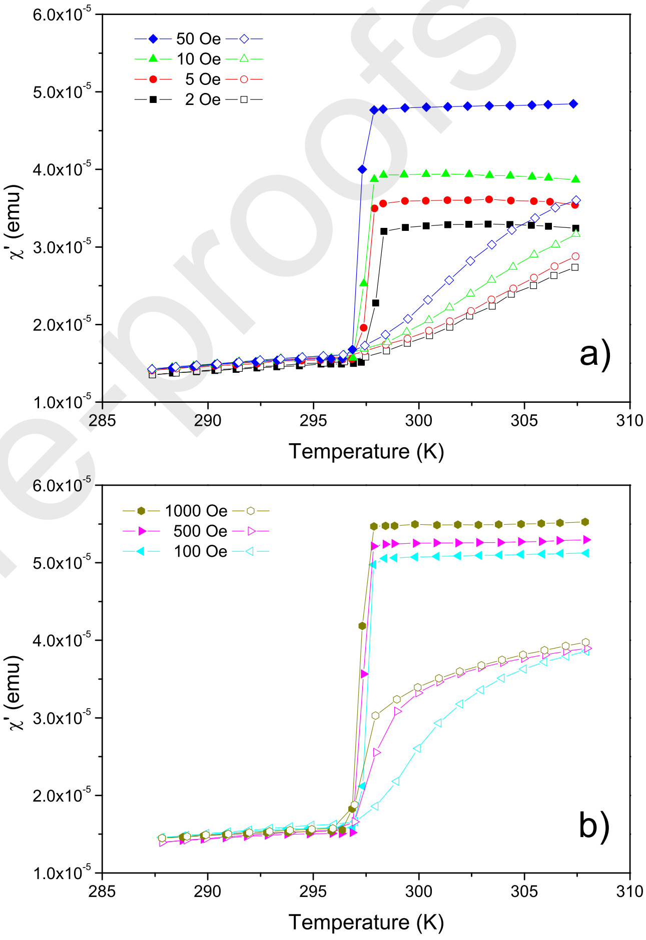

Figure 1: Temperature dependence of the real part $\chi'$ of the *ac* susceptibility for the sample with the volume concentration $\phi_1$=5×10$^{-4}$ in a cooling-heating cycle, with a prior application of a *dc* biasing magnetic field as indicated in the legend. Solid and open symbols correspond to the data obtained on cooling and in heating, respectively.

$\chi'$ suddenly drops. The sudden drop is related to the presence of particles, since the feature is absent in the neat liquid crystal [14]. The magnitude of the sudden reduction $\Delta\chi'$ grows with rising the *dc* bias magnetic field applied in the isotropic phase; $\Delta\chi'$ as well as $\chi'$ are an order of magnitude higher than for ferronematics with lower concentrations [14, 15]. The relative magnitude $\Delta\chi'/\chi'$ of the *ac* susceptibility drop at the isotropic-to-nematic phase transition is significantly larger ($\sim$ 70% when the largest *dc* magnetic field is applied before the measurement) than the highest achievable $\Delta\chi'/\chi'$ for ferronematics with concentrations $10^{-4}$ and $2\times10^{-4}$ ($\sim$10%) [15]. Further cooling in the nematic phase causes only a slight decrease in $\chi'$. Similarly to that, heating in the nematic phase results in a slight increase of $\chi'$. Heating above the nematic-isotropic phase transition temperature, however, causes a considerable, though gradual increment of $\chi'$, indicating a kind of memory effect: the system remembers the previously applied *dc* bias magnetic field (even its magnitude to some extent). This in contrast to the results obtained at a low concentration of MPs, where cooling down the FN into the nematic phase caused an irreversible drop of $\chi'$ without any "memory effect" [14]. One has to note here, that a much smaller, but noticeable increase of $\chi'$ in the isotropic phase during heating has also been found in the FN with the volume concentration of $2\times10^{-4}$ at high *dc* bias magnetic fields (500 Oe and 2000 Oe) [15].

Figure 2 shows the temperature dependence of the real part of the *ac* susceptibility for the FN with the higher $\phi_2=10^{-3}$ volume concentration of MPs. In this case $\chi'$ decreases during the cooling in both the isotropic and the nematic phase and the drop at the phase transition is either significantly smaller (for magnetic fields 10-1000 Oe) or absent (for magnetic field 2 Oe and 5 Oe). In heating the sample, $\chi'$ increases linearly without any change above the nematic-isotropic transition, i.e., in contrast to the FN with lower $\phi_1=5\times10^{-4}$ concentration of MPs, here no "memory effect" is observed as a response to the previously applied *dc* bias magnetic field. On the other hand, as one can see in Fig. 2, the increase of the *dc* bias field contributes to a slight increase of the absolute value of $\chi'$ at a given temperature, even in the nematic phase. Such a dependence on the *dc* bias magnetic field in the nematic phase was not observed at lower concentrations of MPs (see e.g., Fig. 1).

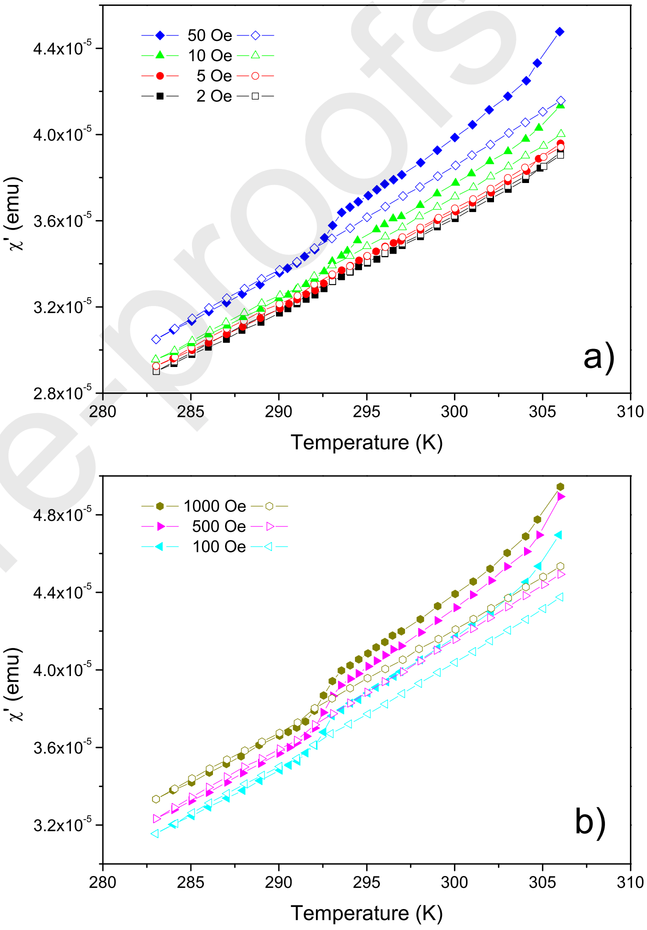

Figure 2: Temperature dependence of the real part $\chi'$ of the *ac* susceptibility for the sample with the volume concentration $\phi_2 = 10^{-3}$ in a cooling-heating cycle, with a prior application of a *dc* biasing magnetic field as indicated in the legend. Solid and open symbols correspond to the data obtained on cooling and in heating, respectively.

## 4. Conclusions

From the results presented here and in our previous works [14, 15], several conclusions can be made on the *ac* magnetic susceptibility of ferronematics made of a specific, 20 nm diameter spherical MPs (Ocean NanoTech) in the matrix of a specific nematic LC, 6CB. Most importantly, we have found that the optimal volume concentration of the MPs is around $\phi \approx 5\times10^{-4}$, for which the largest relative enhancement $\Delta\chi'/\chi'$ is achieved as a response to *dc* bias magnetic fields. For lower $\phi$ concentrations less MPs contribute to the *ac* magnetic susceptibility and, therefore, both the absolute value of $\chi'$, and the enhancement $\Delta\chi'$ have a lower value.

For higher MP concentration, $\phi > 5\times10^{-4}$ presumably the intensified aggregation process of the MPs drastically suppresses (or even terminates) the enhancement of $\chi'$ induced by the *dc* bias magnetic field. To our interpretation, the *dc* bias magnetic field in this case is unable to brake the clusters of MP aggregates with a near-to-zero net magnetic moment [14] and therefore, MPs in these clusters do not contribute much to the enhancement of the *ac* magnetic susceptibility. Naturally, a higher *dc* bias field can break at least partially the MP clusters more efficiently and by that, the slight increase of $\chi'$ with the increase of the *dc* bias (see Fig. 2) can be explained.

The most puzzling observation is made at the concentration $\phi = 5{\times}10^{-4}$ (and to some extent, at $\phi = 2{\times}10^{-4}$ for large *dc* bias magnetic fields $\geq$ 500 Oe [15]), where the largest $\Delta\chi'/\chi'$ changes are detected. Namely, in contrast to the irreversible character of the effect at lower $\phi$ concentrations (where the enhancement $\Delta\chi'$ completely vanishes once the FN is cooled down to the nematic phase), at this concentration upon heating, above the nematic-to-isotropic phase transition temperature a significant, gradual increase of $\chi'$ is measured (see Fig. 1). This gradual increase of $\chi'$ in the isotropic phase indicates that besides the ”trapping effect” of the topological defects in the nematic phase [18], either the time scales (considering the experimental conditions described above), or the temperature-induced fluctuations (eventually both) are also needed for the better understanding of the phenomenon. Therefore, for the future, besides the investigations of the effect on different FN compositions (different MP-type and/or LC matrix), the clarification of this open question is also crucial.

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