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Neutron depolarization and μSR studies of ferrofluids

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This paper has been done to discuss some aspects of using both neutron and μSR techniques in the study of magnetic nanostructures. For this purpose we review our own experience on ferrofluid samples. A brief description of the experimental techniques involved in the neutron and muon measurements is followed by two examples of ferrofluid investigations.

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1. Introduction

Design, manufacture and characterization of materials are nowadays in the top of any activity connected to the development of new technologies. There is no single experimental technique that can provide us with all the information we need to know about materials. Different techniques, based on different physical processes, provide different information, and as the materials under study become ever more complex, it becomes crucial to study them using multiple, complementary experimental technique.

The great penetrating power of the neutron makes it a powerful probe of the microscopic nature of condensed matter which reveals key insights [1-3]. However the value of neutron data can be considerably enhanced by the use of complementary data obtained by other methods [4].

Muon spin relaxation and neutron scattering are two powerful experimental techniques which are used to study magnetic materials. These techniques share some common features: they are both representative experimental methods which use large accelerator or reactor facilities for condensed matter physics; they are both direct microstructure methods, in contrast to bulk measurements. The μSR and neutron scattering have, however, various complementary characteristics: different time window for dynamic phenomena; short-range point-like in real space vs. a probe in reciprocal space which reflects long-range correlations; a tool to detect static magnetic order vs. a probe to determine its spin structure.

In this paper, we discuss some aspects of using neutron depolarization and muon spin relaxation techniques in the study of magnetic nanostructures. For this purpose we review our own experience on ferrofluid samples. A brief description of the experimental techniques involved in the measurements is followed by two examples of the investigations of ferrofluids.

2. Experimental

2.1. Sample description

The ferrofluids represent colloidal suspensions of single domain ferromagnetic particles of about 100A in diameter, stabilized with surfactant molecules, in a suitable liquid carrier [5-7]. From a magnetic viewpoint, the ferrofluid is very similar to the ferromagnetic materials with respect to the fact that small magnetic moment regions are randomly distributed in absence of an external magnetic field. The magnetic regions in the former are the magnetic colloidal particles, while those of the latter are the magnetic domains. There are, however, great differences between them. First, the magnetic domains are micrometer sized and widely distributed. On the contrary, the colloidal particles are smaller, which consequently, generates statistical phenomena because of the law of large numbers in the statistics. Therefore, though the particle sizes are distributed log - normally [8], it is permitted to assume that all the particles are spheres of the same radius. Secondly, the interactions between the colloidal particles in non-concentrated ferrofluids are estimated to be week in comparison to the strong magnetic interaction between the magnetic domains in ferromagnetic materials.

2.2. Neutron depolarization (ND)

It is known that depolarization of the transmitted neutron beam through magnetic media occurs mostly by interaction with the inhomogeneity on mesoscopic scale, and it can be well treated by integration of the process that polarized neutrons go through in local magnetic fields. The depolarization wavelength dependence of the of neutron beams transmitted through a ferromagnetic thin plate was originally calculated by Halpern and Holstein [9]. The wavelength dependence is obtained by using polychromatic beams of pulsed polarized neutrons. First experimental application of the neutron depolarization was done by

Burgy et.al. [10]. At present, this method is developed and exploited at a few places in the world [11- 33], due to Rekveldt [15, 21, 26] works of neutron depolarization (ND) in ferromagnetic materials. A ND experiment in general yields the mean size of the magnetic inhomogeneities along the neutron path (the "magnetic correlation length"), and the mean magnetization. The range of magnetic correlation lengths which can be measured covers 10 nm to mm's, making ND to some extend complementary to small-angle neutron scattering (SANS).

We consider the polarized-neutron passage in magnetic medium where the beam cross section is pretty narrow. Along the neutron path the internal magnetic field can be defined by B(r). To make it simple it can be considered that all of the incident neutron-polarization vectors P_i are polarized along the z direction. After the neutrons enter the magnetic medium, the polarization vector P starts to precess around the local field B(r). The motion of P just follows the simple classical equation of motion,

$$\frac{dP}{dt} = \gamma P \times B(r)$$

where γ is the neutron gyromagnetic ratio and r is the coordinate along the flight path, which is related to the neutron velocity v by v = r/t.

In neutron depolarization (ND) experiment the polarization vector of a polarized neutron beam is analyzed after the transmission through magnetic medium. During the transmission the polarization vector is affected by the local magnetization of the medium. Mean magnetic induction results in net processional motion (Larmor precession) of the polarization vector around the former, while magnetic inhomogeneities result in shortening of the z - component (z paralel to direction of the magnetic field) of the polarization vector, named depolarization henceforth.

For a superparamagnetic system we assume that the Larmor precession essentially takes place within a ferromagnetic cluster. The observed $P(\lambda)$ polarization shows an oscillation with request to the neutron wavelength:

$$P(\lambda) = P_0 + (1 - P_0)\cos(H\lambda) \qquad (1)$$

where P_0 is given by $P_0 = \left\langle \frac{B_\parallel^{\,2}}{B^2} \right\rangle_B$, representing how the ferromagnetic clusters align along the applied field. H is the field integral and is expressed as

$$H = cB\left\langle (\delta_1 + \delta_2 + ...)\right\rangle_{path} \qquad (2)$$

2.2. μSR

The polarized muons are implanted into the sample where they stop. The spin of the muon in the sample undergoes the Larmor precession in the magnetic field. Distribution of the local magnetic fields leads to depolarization of the muon ensemble. In the sample, the positive muons (we used a bunch of positive muons) decay according to the process $\mu^+ \to e^+ + \overline{\nu}_e + \nu_\mu$ with a mean lifetime of 2.2 μs. Positrons are preferentially emitted along the instantaneous muon spin direction. The observed asymmetry of angular distribution of the decay of positrons is a direct way to measure the muon polarization. Each implanted muon and resulting positron is detected by a system of scintillation counters. During the time interval of ≈ 10 μs only those $\mu^+ \to e^+$ decay events were analyzed, which satisfy the condition where there is a corresponding decay positron for each incoming muon.

The positron decay distribution function over time can be approximate with

$$N(t) = N_0\left[1 + P(t)\right]e^{-t/\tau_\mu} + \mathrm{D} \qquad (3)$$

where, N_0 is the normalization factor, $P(t)$ is muon depolarization function and τ_μ is the free muon lifetime.

3. Results and discussion

3.1 ND experiments

In our experiment [32, 33], performed at the SPN spectrometer in function at IBR-2 reactor, it was measured: P(H), neutron-beam polarization at the outlet of the analyzer after the neutron beam transmission through the sample and separately $P_0(H)$, neutron-beam polarization at the outlet of the analyzer after the neutron beam transmission through an empty sample holder, as :

$$P(H,\lambda) = [R(H, \lambda) - 1]/[R(H, \lambda) + 1]$$

$R = I_{off}/I_{on}$, and I_{off} and I_{on} are the integral intensities over the (0.5 ÷ 15) A wavelength range registered by the neutron detector in the case the spin - flipper is off and on, respectively. P_0 is the multiplication between p_1 and p_2, where p_1 and p_2 represent the polarizing efficiency of the polarizer, respectively of the analyzer. The quantity characterizing the depolarization process in a sample, P/P_0 is obtained after several calculations from the reflected intensities into the detector.

The normalized intensity of neutrons is analyzed as:

$$I = (I_{on} + I_{off}) / I_{on,0} + I_{off,0})$$

The measurements were done on a sample Fe_3O_4 ferrofluid in transformer oil.

Fig.1 shows the plot of the normalized intensity of transmitted neutrons $(I_{on} + I_{off})/(I_{on,0} + I_{off,0})$, versus the magnitude of the external magnetic field in the range of (0 ÷ 3.6) kOe for the case of 17.5% particle volume concentration. For the magnitude H = 130 Oe of the magnetic field, it can be seen a minimum of the intensity, which corresponds to the rising of the neutron scattering. Also, for this magnetic field, Fig.2 shows that the neutron positive spin state scattering is bigger than those corresponding to the negative spin state. This means that there is interference between the nuclear and magnetic scatterings. Thus, the intensity of the magnetic field is bigger when the nuclear potential variation over its mean value is positive. For 2 A wavelength the scattering of the negative spin state is 15% and of positive state 25%. One can conclude from this that the variation of the magnetic potential is 12.5% of the magnitude variation of the nuclear potential.

The variation of the intensity of the magnetic field H can be determined from the variation of the nuclear potential (nuclear contrast). The value of the magnetic correlation length can be determined from the geometry of the experiment ($L = \left\langle (\delta_1 + \delta_2 + ...) \right\rangle_{path}$, where L is the sample thickness). In our case it is about 300 A.

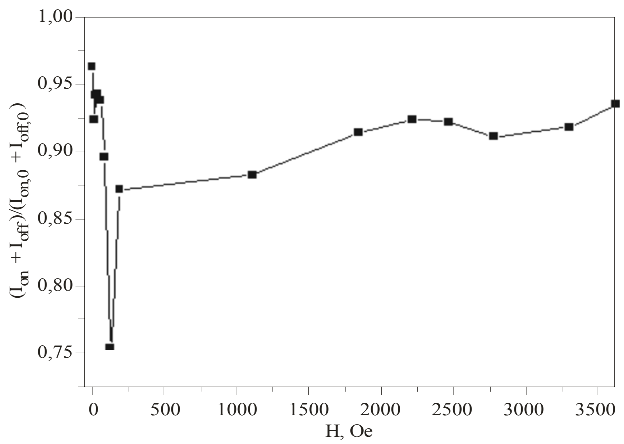

Fig1 The normalized intensity of transmitted neutrons, expressed in n/st (neutrons/starst, where starts represents the number of pulses of the reactor and is considered as a unit of time), versus the magnitude of the external magnetic field.

This value is 3 times bigger than the particles diameter. So, this means that there exists aggregation in clusters containing dozens of particles. The existence of big clusters is proved by the fact that the sample reached the magnetization saturation for small values of intensity of the magnetic field, about 3 Oe.

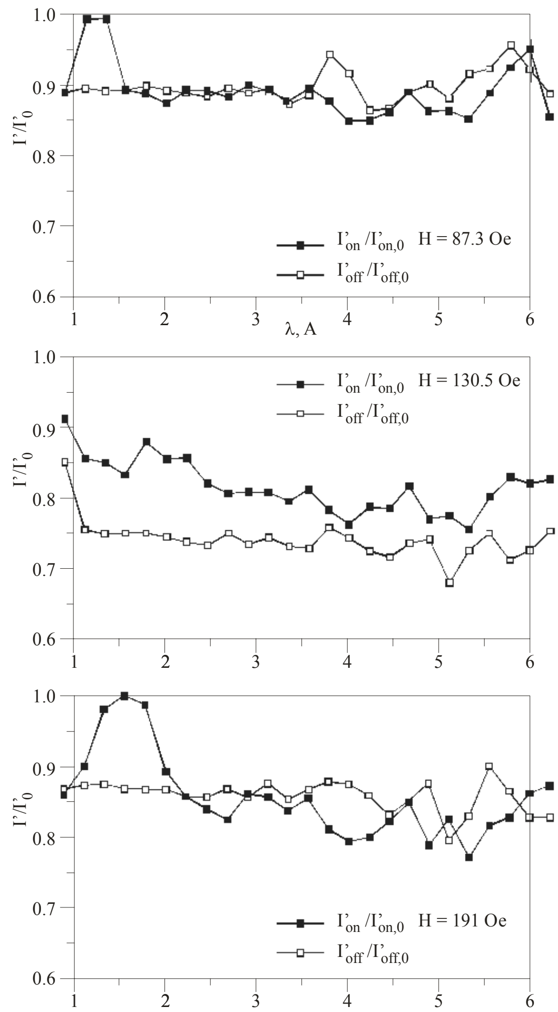

Fig.2 The dependence of the normalized intensity (for the spin -flipper "off" and "on" versus the wavelength of neutrons for three values of the magnetic field: 87.3 Oe; 130.5 Oe; 191 Oe.

For bigger values of the intensity of the magnetic field the scattering decreases. The fact can be explained by the magnetic contrast decrease between the clusters and the interclusters gaps.

3.2 μSR investigations

The measurements were accomplished at the muon channel of the Phasotron in function at the JINR Dubna, at the MUSPIN experimental facility [34].

The investigated sample was the D_2O based ferrofluid with 4.7% volume concentration of Fe_3O_4 particles double stabilized with dodecylbenzenesulphonic acid (DBS).

Our measurements were performed in two conditions:

(i) in a magnetic field transversal relatively to the muon spin direction (TF) and

(ii) in zero magnetic field (ZF), respectively.

The temperature range of the measurements was 114 K ÷ 300 K.

In the case of measurements in magnetic field, the depolarization function obtained to fit the experimental TF μSR data (Fig.3), is given by relation:

$$P_{TF}\left(t\right)=P_0 e^{(-\sigma t)}\cos\left(\omega t+\varphi\right) \qquad (4)$$

, where P_0 is the apparent initial asymmetry, σ is the relaxation rate (responsible for slow depolarization by random local fields), ω is the muon Larmor frequency, $\gamma_\mu = ge/2m_\mu$ is the gyromagnetic ratio for the muon, φ is the apparent initial phase of the precession.

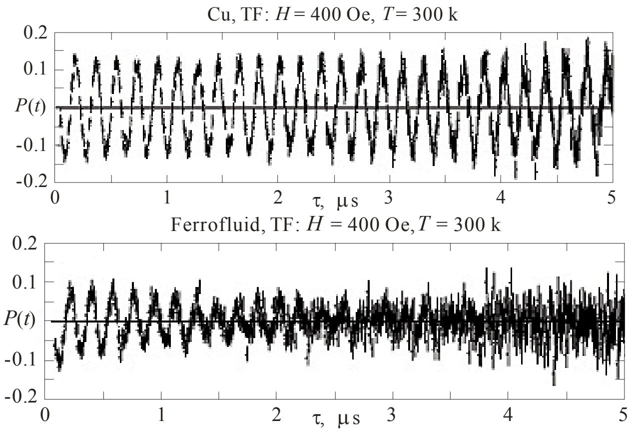

Fig.3 The μSR–spectra for copper (up) and ferrofluid samples in an external magnetic field of 400 Oe, transversal to the muon spin direction (down), with background and muon lifetime corrections.

The best fit of the experimental data measured in the zero magnetic field (ZF), for all the temperature range is obtained with $P_{ZF}\left(t\right)$ function, where $k=1$

$$P_{ZF}\left(t\right)=P_0 e^{\left(-(\sigma t)^k\right)} \qquad (5)$$

These surprising results are obtained probably due to the detection of signal mixture from the muons stopped in all the components of the ferrofluid system.

Each of the fitted parameters in equation (3) is of special interest in certain studies. The precession frequency, $\omega=\gamma_\mu B_\mu$. and the relaxation rate σ, give a direct quantitative measure of the inhomogeneity δB_μ of the local field B_μ at the muon site.

A significant muon polarization relaxation was observed at temperature of 300K, in a magnetic field from 100 Oe to 700 Oe transversal to the muon spin direction (see Fig.3), as well as at temperatures less than 114 K, and higher than 250 K, in zero magnetic field (see Fig.4) [35, 38].

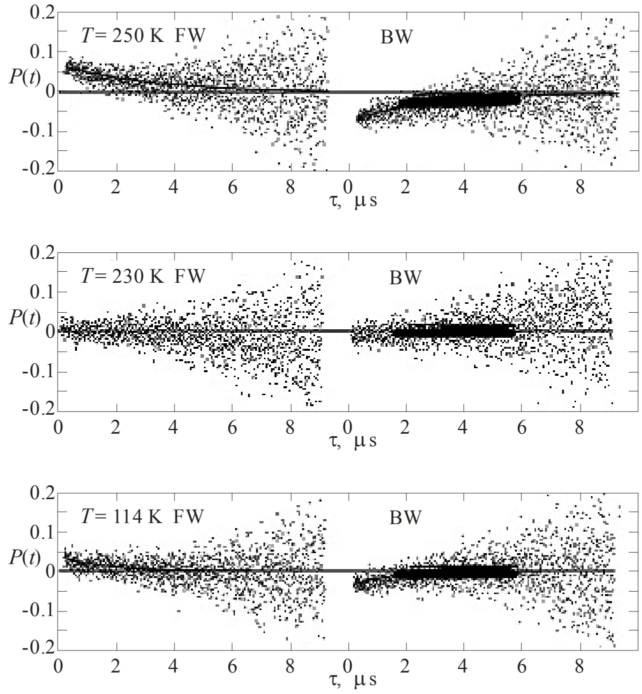

Fig.4 μSR–spectra for the ferrofluid sample in zero magnetic field, for temperature values of 114 K; 230 K; 250 K (with background and muon lifetime corrections).

The missing asymmetry, as it happens at T=230 K, usually represents a rapid depolarization of particles, i.e. muons, less than the dead time of the spectrometer (~10ns).

In Fig.5 and Fig.6 the temperature dependence of muon polarization amplitude P_0 and of the muon relaxation rate σ obtained in zero field are plotted. The dependence shows a complicated behavior.

The origin of that behaviour is not yet understood at the present. As it was reported earlier for bulk and monocristaline Fe_3O_4 [36, 37], such anomalies are associated with magnetite properties and may be precursor of the Verwey phase transition.

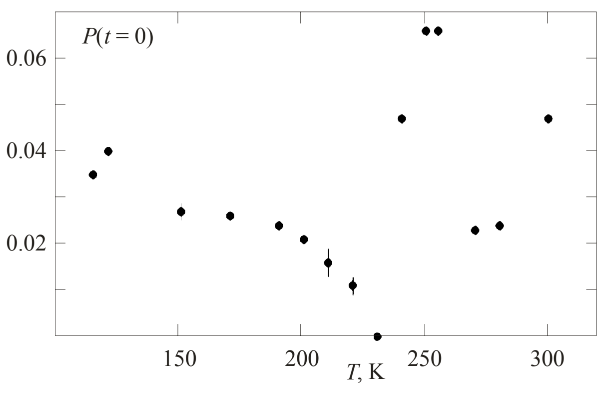

Fig.5 Muon polarization amplitude vs .temperature, P(T) in zero field.

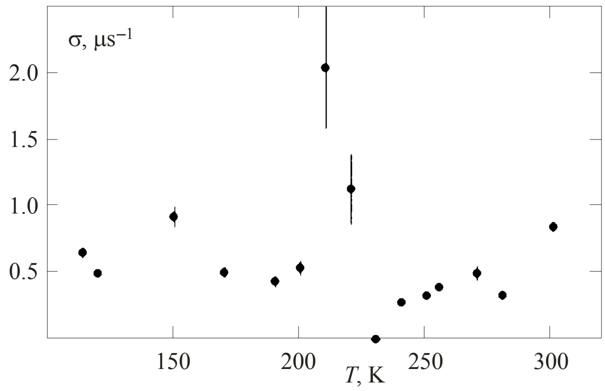

Fig.6 Muon relaxation rate vs .temperature, σ (T) in zero field.

The average field inhomogeneity at the muon was estimated from the muon spin relaxation rate data, considering that the muon diffusion is zero and the magnetic moments of the nanoparticles are "frozen". In this case, it was shown that, the muon in the sample detects a magnetic field for which the average field inhomogeneity is

$$\delta B = \sigma/2\gamma_\mu = 20G$$

where, $\gamma_\mu = 13.55$ kHz/G.

It must be underlined the fact that what it is seen by μSR in this sample is mostly the signal from the muons stopped in the liquid. Further experiments must be performed to investigate the influence of the particles on the μSR signals.

Also, when positive polarized muon is stopped in H_2O or D_2O, two signals are detected. One of them is due to the formation of muonium (Mu), a hydrogen-like atom, formed from a muon an electron (μ^+e^-), which are precessing with the Larmor frequency determined by the magnetic moment of the electron. The other is due to the positive muon stopped in a diamagnetic environment. For each of them the mentioned earlier measured values can be obtained by the μSR-method. Here are analyzed and compared with those from pure D_2O just the signals from muon. In further work, both signals will be investigated.

4. Conclusions

The basic goal of the depolarization experiments is to observe the magnetic field integrated along the beam path in magnetic medium. This observation can be made because neutron travels with a precession described by the Larmor frequency.

In this sense the method is similar to muon-spin rotation. The essential difference between these two methods is that neutrons travel through the sample while muons are trapped at certain sites in the sample. Therefore the local magnetic field detected by neutrons spins is integrated. All the local information is automatically averaged out, but the data still contain useful information.

It was found out from neutron depolarization measurements, that the ferrofluids with magnetite particles present different effects of magnetic aggregation, dependent on the magnitude of the external magnetic field.

The μSR-method can help to understand magnetic phenomena peculiarities in the systems containing nanomagnetic objects by determining the local magnetic fields in the sample. In the present case, the average field inhomogeneity at the muon site in a ferrofluid sample with 4.7% Fe_3O_4 particle volume concentration was estimated. Further experiments to investigate the particle concentration influence on μSR signals and to analyze both the signals from muon and muonium fractions are required to be performed.

Also, it would be interesting to continue on the same samples both ND and μSR experimental studies with modeling techniques development.

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