

Magnetic properties investigation of a ferrofluid with cobalt ferrite nanoparticles using polarized muons

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μ SR-spectroscopy method was applied to the investigation of water based ferrofluid samples with 0.5% and 3% vol. concentrations of CoFe_2O_4 nanoparticles. The measurements were overdone in the (26 \div 300) K temperature range in an external magnetic field transversal to the muon spin and with the sample cooling: (i) without applied magnetic field (ZFC) and (ii) in the presence of field (FC). It was found that regardless of the cooling regimes in both samples the diamagnetic (muon) fraction in ferrofluid is produced approximately in the same ratio as well in pure H_2O . However, the relaxation rate and the precession frequency of the muon spin in the ferrofluid with 3% nanoparticles concentration depends on the cooling conditions of the sample, and they differ significantly from similar data for H_2O . The present results show that magnetic nanoparticles of cobalt ferrite have a high coefficient of magnetic anisotropy. The magnetic field, created by single domain nanoparticles in ferrofluid has been found.

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1. Introduction

In connection with the development of systems with new properties, important for practical applications, significantly increased the interest in the study of nanostructured materials. Among them a special place occupies materials in which magnetic nanoparticles are distributed in a nonmagnetic medium. Such materials include ferrofluids, ultrastabilized suspensions of single domain magnetic nanoparticles (usually, Fe_3O_4 , CoFe_2O_4 , etc) in a liquid medium (see e.g. [1, 2, 3, 4, 5]).

Currently widely studied are magnetic fluids on the basis of nanoparticles of spinel ferrites MeFe_2O_4 (Me is Mg, Cr, Mn, Fe, Co, Zn) dispersed in organic or inorganic liquid environments. Stability of magnetic fluids is achieving by coating magnetic nanoparticles by a surfactant (surface active substance), that prevent them from sticking together due to the van der Waals force and the magnetic dipole-dipole interactions. Below the Curie temperature for MeFe_2O_4 each of nanoparticles has a magnetic moment, close to the total moment of molecules in the particle. Stability of magnetic fluid in water is usually present at low nanoparticle concentrations (<5-7%).

Cobalt ferrite CoFe_2O_4 is known to have cubic magneto-crystalline anisotropy with the highest anisotropy constant among the ferrites [6]. The Curie temperature for cobalt ferrite equals 793 K.

Magnetic properties of ferrofluids were studied by means of different instruments and methods, including the

quantum magnetometers (SQUID), Mossbauer spectroscopy [4,7], small-angle neutron scattering [8,9,10,11,12].

We have used polarized positively charged muons to study the magnetic properties of the ferrofluids. The spatial distribution of positrons from the decay of polarized muons $\mu^+ \rightarrow e^+ + \nu_e + \tilde{\nu}_\mu$ is asymmetric with respect to the initial muon-spin polarization because of parity violation. In matter, the polarization of the muon depends on the interaction of its magnetic moment with the environment, including with local magnetic fields. Change the polarization of the muon in time can be experimentally investigated by monitoring the time-dependent spatial asymmetry of positrons from $\mu^+ \rightarrow e^+$ decay [13].

When polarized positive muons stopped in water, as a rule, two kind of μ SR signal will be detected. One of them arises from muonium (Mu) – a hydrogen-like atom [14, 15, 16], consisting of a muon and an electron (μ^+e^-). The magnetic moment of the muonium as the sum of magnetic moment of the electron and muon is precession in a magnetic field with the Larmor frequency Ω . Another signal refers to either the free muon or the muonium that is included in the composition of the diamagnetic compound. In the diamagnetic compound the magnetic moment of muon is precession in a magnetic field as magnetic moment of a free muon with a frequency ω . The ratio of the precession frequencies is equal to $\Omega/\omega \approx 103$. The results of the μ SR studies at the “weak” and “strong”

magnetic fields for the $\text{Fe}_3\text{O}_4/2\text{DBS}/\text{D}_2\text{O}$ (suspension ferrite nanoparticles in D_2O stabilized by double layers of dodecyl benzene sulfonic acid) sample were analyzed in [17, 18, 19, 20, 21]. In present experiments muonium component was not observed because of high precession frequency of its magnetic moment in "strong" magnetic field and of limited time resolution of the equipment. In this work are presented the temperature dependences of the muon spin polarization, relaxation rate and precession frequency in ferrofluids based on a suspension of nanoparticles of CoFe_2O_4 in water.

2. Measurements

The studied ferrofluids was a suspension of nanodispersed cobalt ferrite (CoFe_2O_4) in water stabilized by the double layers of surfactant. The sample (S1) with the 0.5% volumetric concentration of magnetic particles stabilized with dodecyl benzene sulphonic acid was produced by Dr. D. Bica (CFATR, Romanian Academy-Timisoara Division, Timisoara, Romania). Second sample (S2) with concentration of nanoparticles of 3.0% was synthesized at Institute of Technical Chemistry of Ural Division of RAS [22, 23, 24, 25]. Nanoparticles were covered by layers of sodium dodecyl sulfate (DDS-Na) and of lauric acid (LA). One ml of S2 sample contain 0.17 g cobalt ferrite and there was 0.25 g surfactant for 1 g of CoFe_2O_4 .

The morphology and microstructure of the $\text{CoFe}_2\text{O}_4/\text{LA}/\text{DDS-Na}/\text{H}_2\text{O}$ ferrofluid sample treated in 'Biofuge 15R' (Heraeus instruments) 2 fold at 6000 rot/min for 60 min. High-resolution TEM (HRTEM) analysis was carried out on a LEO 912 AB OMEGA transmission electron microscope with an accelerating voltage of 120 kV (at Advanced Technology Centre, Moscow). One droplet of water dispersion of CoFe_2O_4 nanoparticles was dropped on a carbon-coated copper grid and then dried naturally before recording the micrographs. The measured size distribution of nanoparticles for sample S2 presented on Fig.1. The experimental data was approximated with log-normal distribution.

$$f(D) = \frac{1}{D\sigma(2\pi)^{0.5}} \cdot e^{-\frac{(\ln(D)-\ln(D_0))^2}{2\sigma^2}}$$

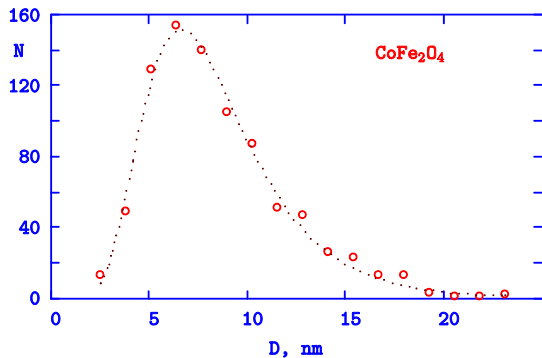


Fig.1 The size distribution of the CoFe_2O_4 nanoparticles for sample S2.

The dashed line corresponds to final approximation with value of parameters log-normal distribution: $D_0=7.8\pm 0.1$ and $\sigma=0.40\pm 0.01$ with mean value.

$$\bar{D} = D_0 \exp(\sigma^2/2) = 8.5 \text{ nm} .$$

The μSR experiments were performed at a polarized muons beam channel of the synchrocyclotron of the Petersburg Nuclear Physics Institute. The muon beam polarization was about 90%. The measurements were carried out at the μSR setup [26]. The sample was located in a magnetic field transverse with respect to the muon spin direction. The magnetic field created by Helmholtz coils presents uniformity in the central volume of 200 cm^3 better than 10^{-4} . Earth's magnetic field and scattered field from surrounding magnetic materials was reduced to 0.05 G by additional solenoids. The samples were introduced into a cryostat and cooled by liquid helium vapor. The temperature of the samples was stabilized with an accuracy of 0.1 K.

The samples were packaged into a cylindrical copper cell 80 mm in diameter and 10 mm in height. The cylinder axis was oriented parallel to the muon beam axis. The external magnetic field was perpendicular to the cylinder axis. The density of the studied material in the beam direction was about 1.17 g/cm^2 . The measurements were carried out in the temperature range of $26 \div 300 \text{ K}$.

The time between the stopping of muon in the sample and the appearance of the positron was measured with a "time-digital" convertor (TDC) with the range of direct conversion $10 \mu\text{s}$ and a channel width of 5 ns. The data acquisition rate of "good" events in the histogram was about 200 s^{-1} . Typically, about one million events were accumulated in a histogram.

The experimental data were fitted with the function

$$N(t) = N(0) \cdot e^{-\frac{t}{\tau(\mu)}} \left[1 + b \frac{P_0}{3} \cdot e^{-\lambda t} \cdot \cos(\omega \cdot t + \varphi) \right] + B \quad (1)$$

$\tau(\mu) = 2.197 \mu\text{s}$ is the positive muon lifetime; P_0 , λ , ω and φ are the initial polarization, relaxation rate, precession frequency and phase of the muon spin respectively; B is the background; and b is the constant dependent on the measurement facility parameters (b is close to 1)[27].

The amplitude of the muon spin precession in the samples was compared with the precession amplitude in a copper sample for which the positrons asymmetry coefficient from the muon decay was $a=b \cdot (P_0/3) = 0.308 \pm 0.003$ in a transverse magnetic field of 525 G.

3. Results and discussion

The parameters a , λ , ω and φ of muon polarization were found by approaching the function (1) to experimental data by least squares method. Temperature dependences of muon spin relaxation rate, amplitude and precession frequency in a magnetic field for samples with 0.5% and 3% nanoparticle concentration are presented on Fig.2 and Fig.3, respectively. Apparently, for sample with

concentration magnetic nanoparticles of 0.5% the precession amplitude a practically coincides with its value in "pure" (bi-distilled) water and does not depend on the cooling conditions of the ferrofluid (FC- sample is cooled in magnetic field, ZFC - sample is cooled first in absence of magnetic field and then the magnetic field is switched on). Measurement of "pure" water was done in FC conditions. Changing asymmetry (diamagnetic fraction of polarization) at 125 K and 273 K in D₂O and H₂O were studied earlier in [14,15,16]. In particular at 273 K the increase of the asymmetry is due to solid-liquid phase transition.

In the FC measurements the muon spin relaxation rate in ferrofluid sample systematically is a little above, while the muon spin precession frequency is less, than in water. In case of ZFC measurements the muon spin precession frequency is close to its value in water. The above specified distinctions are more pronounced in the case of 3.0% nanoparticle concentration ferrofluid sample.

The magnetic properties of the ferrofluids depend on the ratio of the magneto-crystallographic anisotropy energy E_a to the thermal fluctuation energy kT of the magnetic moment, as well as on the external magnetic field magnitude. If the single domain nanoparticle has a uniaxial anisotropy, its magnetic anisotropy energy is equal to

$$E_a = K_I \cdot V,$$

where K_I is the anisotropy constant and V , the volume of a nanoparticle. If $K_I \cdot V \gg kT$, the nanoparticle magnetic moment is oriented along the easy magnetization axis. There are possible transitions between two opposite directions of the magnetic moment, relative to the easy axis of magnetization. It has been shown by Neel that the frequency of these transitions depends on temperature as [28] (see also [2, 4]):

$$f = f_0 \exp(-K_I \cdot V/kT)$$

In case of FC measurements the magnetic moments of nanoparticles are ordered due to the external magnetic field and in sample the magnetic field magnitude differs from that of the external field. Therefore, the relaxation rate and the precession frequency of a muon spin in the medium will depend on the sum of the external magnetic field, the nanoparticles created field and its dispersion. The fact that in case of FC measurements the frequency and relaxation rate of a muon spin practically do not depend on temperature (see Fig.2 and Fig.3), testifies to the insignificant influence of Neel transitions on the magnetic field created by the nanoparticles.

In case of cooling the ferrofluid in absence of a magnetic field (ZFC) the easy magnetization axis and the magnetic moment of nanoparticles are freezed in space in random direction.

Hence, the mean magnetic field created in fluid by the nanoparticles, will be equal to zero. An external magnetic field can order the nanoparticle magnetic moments of nanoparticles if the interaction energy of nanoparticle with the magnetic field surpasses the indispensable energy for

turning the nanoparticle magnetic moment by an angle ϑ [29]:

$$E = K_I V \sin^2 \vartheta,$$

where ϑ is an angle between the easy magnetization axis of a nanoparticle and the external magnetic field.

It was found that a constant of magnetic anisotropy for CoFe₂O₄ nanoparticles is the same as for bulk samples, and it is exponentially decreases with temperature increasing [6]:

$$K_I = K_I(0) \exp(-1.9 \cdot 10^{-5} T^2)$$

The value $K_I(0)$ for nanoparticle sizes of 32 nm, practically coincides with the value for crystalline samples and is equal to [6]: $K_I(0) = 1.02 \cdot 10^7 \text{ erg/cm}^3$.

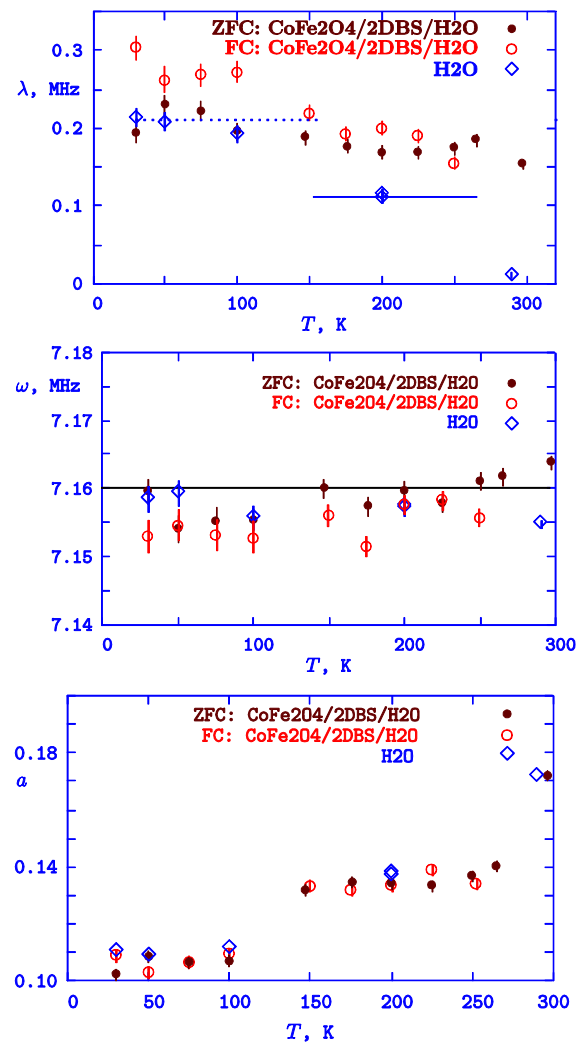


Fig. 2 The temperature dependence of muon spin precession amplitude (a), frequency (ω) and relaxation rate (λ) in the sample S1 (0.5% concentration of CoFe₂O₄ nanoparticles in H₂O) measured in magnetic field $B \approx 525$ G.

Since the magnetic anisotropy energy of a single domain nanoparticle is proportional to its volume, the magnetic field indispensable for ordering their magnetic moments, will depend both on temperature and the size of nanoparticles. Therefore, in case of ZFC measurements, at low temperature, when $K_1 \cdot V > kT$ and the interaction of the nanoparticle with the external magnetic field is insufficient for overcoming

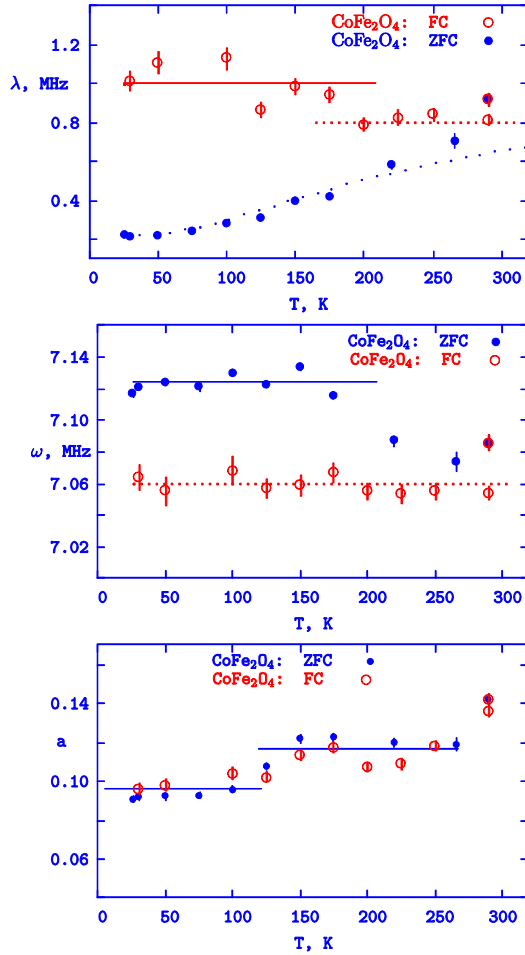


Fig.3 The temperature dependence of amplitude, frequency and relaxation rate of the muon spin precession in sample S2 (3% concentration of CoFe_2O_4 nanoparticles in H_2O) measured in magnetic field $B \approx 525$ G.

the magnetic anisotropy barrier E_a , the mean magnetic field created by the nanoparticle magnetic moments in the environment is equal to zero and the relaxation rate of magnetic moments is negligibly small. Accordingly, in the ferrofluid the values of muon spin relaxation rate and precession frequency are close to those in water. With temperature increasing the anisotropy constant decreases, and, in an external magnetic field gradually there appears an ordering of the particle magnetic moments depending on their sizes. Hence, the muon spin relaxation rate and the precession frequency will approach to their values observed in the FC conditions. We will notice that at temperatures below ferrofluid freezing values (that practically equals to the freezing temperature of water) no rotation of the nanoparticles is obviously possible.

Using the average value of the muon spin precession frequency within the temperature range of $30 \div 250$ K in FC measurements and $26 \div 175$ K in ZFC measurements (see Fig.3), it was found that in an external magnetic field of 525 G, the nanoparticles create in sample S2 an additional magnetic field of about $B = (\omega(\text{ZFC}) - \omega(\text{FC})) / \Gamma_\mu = 4.7 \pm 0.2$ G (Γ_μ , the gyromagnetic ratio for the muon is equal to 0.01355, (ω is in MHz, B is in G).

From the Fourier analysis of μSR data it follows that in the ferrofluid the magnetic field differs from the external field not only in magnitude but also holds an increase in its dispersion. As it can be seen from Fig.4, the peak position, in the case of sample S1 of 0.5% CoFe_2O_4 nanoparticles at FC measurements and for sample S2 of 3.0% CoFe_2O_4 nanoparticles in ZFC measurements, coincides with that for copper, and for the ferrofluids the line somewhat is broadened. In the case of FC measurements it appears a significant broadening and shift of the line in ferrofluid relative to that in copper.

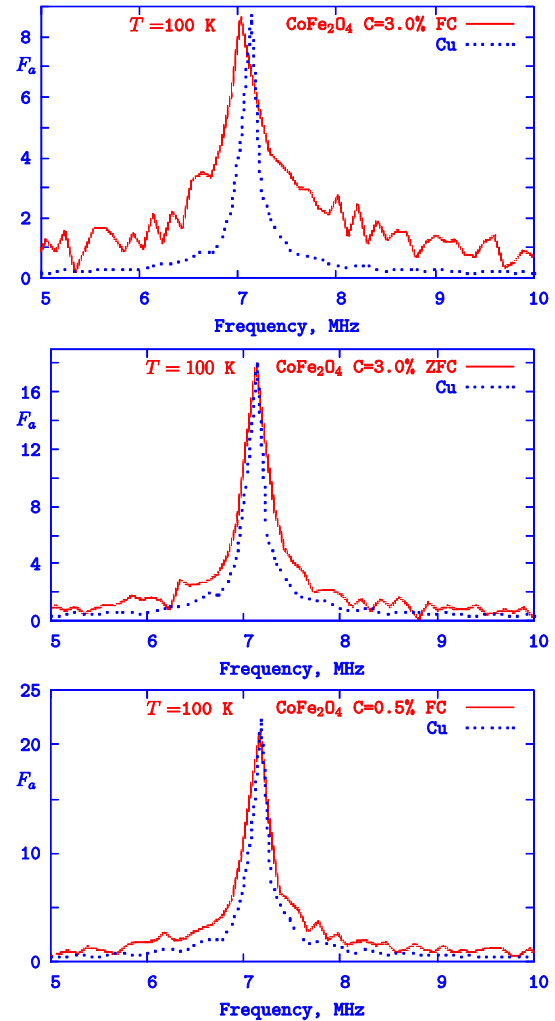


Fig.4 The results of Fourier transformation of μSR data for Cu and for samples with concentration of the cobalt ferrite nanoparticles of 0.5 % (S1) and of 3% (S2). The samples with cobalt ferrite nanoparticles were measured at 100 K in FC and ZFC condition.

In Tab.1 the Fourier spectra line width of μ SR data for ferrofluids is compared with similar data for copper and water. In the water, the line is broadened by about 30% compared to the copper. There is an about 23% broadening of the line in the case of ZFC for the sample S2 in comparison with water. The greatest broadening of the line (85%) in ferrofluid sample S2 compared to water is observed at the FC measurements.

Table 1 Full width of the line at half max (FWHM) in Fourier spectrum for μ SR data at copper, water, and at samples S1, S2 with a concentration of CoFe_2O_4 in water $C=0.5\%$ and 3.0% , respectively.

sample	C, %	T, K	FC/ZFC	FWHM, MHz	λ , MHz
Cu	100	300	-	20	0.00±0.01
H ₂ O	100	100	FC	26	0.19±0.01
CoFe ₂ O ₄	0.5	100	FC	30	0.27±0.02
Cu	100	300	-	20	0.00±0.01
CoFe ₂ O ₄	3.0	100	ZFC	32	0.29±0.02
CoFe ₂ O ₄	3.0	100	FC	48	1.23±0.06

From comparison of the temperature dependence of the relaxation rate and frequency shift of the muon spin recession frequency for the cases ZFC and FC measurements it follows that at temperatures below 170 K interaction magnetic moment (m) of the nanoparticles with external magnetic H is not able to overcome magnetic anisotropy barrier at ZFC: $mH < K_1V$. Therefore it follows that cobalt ferrite nanoparticles with size ≈ 8.5 nm (with about $4 \cdot 10^3$ molecules of CoFe_2O_4 in nanoparticle) have a large magneto-anisotropy constant. Also it follows that, the Neel mechanism of fluctuations of the magnetic moments is negligible until room temperature. However, based on the measured distributions by size of particles and magnetic anisotropy constants for the nanoparticles with dimension 32 nm, one might expect the degree of ordering of the magnetic moments in ZFC measurements should be approached close to that in FC at higher temperatures than it observed in the present experiment. Therefore, it must be assumed that the magnetic anisotropy constant of the nanoparticles is changing with decreasing size.

4. Conclusions

Magnetic properties of ferrofluids with 0.5% and 3.0% CoFe_2O_4 magnetic nanoparticles concentration in water have been studied in a wide range of temperature by μ SR method. These results evidence that single domain nanoparticles with dimension about 8.5 nm have a high anisotropy coefficient. In case of ferrofluid with 3.0% nanoparticle concentration cooled in external magnetic field of 525 Oe, a nanoparticle creates in medium an additional magnetic field of 4.7 Oe. Also the indication

that the magnetic anisotropy coefficient changes with the nanoparticles size decreasing is obtained.

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