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μSR Study of the Properties of Fe_3O_4-Based Nanostructured Magnetic Systems

M. Balasoiu[a, c], S. G. Barsov[b], D. Bica[d], L. Vekas[d], S. I. Vorob'ev[b], K. I. Gritsaj[a], V. N. Duginov[a], V. A. Zhukov[a†], E. N. Komarov[b], V. P. Koptev[b], S. A. Kotov[b], T. N. Mamedov[a], C. Petrescu[d], and G. V. Shcherbakov[b]

[a] *Joint Institute for Nuclear Research, Dubna, Moscow region, 141980 Russia*
e-mail: duginov@nusun.jinr.ru
[b] *Petersburg Nuclear Physics Institute, Russian Academy of Sciences, Gatchina, Leningrad region, 188300 Russia*
[c] *Horia Hulubei National Institute of Physics and Nuclear Engineering, Bucharest, 76900 Romania*
[d] *Center for Fundamental and Advanced Technical Research, Timisoara, 300223 Romania*
[e] *R&D Institute for Electrotechnics, Bucharest, 74204 Romania*

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A ferrofluid based on Fe_3O_4 nanoparticles dispersed in heavy water D_2O is studied using the μSR method. The experiment has been carried out at temperatures 26–300 K. It is found that the diamagnetic (muon) fraction is formed in the ferrofluid in about the same amount as in D_2O, but the muon-spin relaxation rate in the ferrofluid is much higher than in D_2O. A significant shift of the muon-spin precession frequency in the ferrofluid is observed. It is shown that the shift of the muon precession frequency as a function of the external magnetic field is described by the Langevin function typical of paramagnetic magnetization. The mean magnetic field in the medium due to magnetic-nanoparticle polarization in an external field is experimentally determined. The nanoparticle sizes are estimated.

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INTRODUCTION

Interest in studying nanostructured materials has grown significantly in recent years. A special place among such materials is held by nonmagnetic media containing magnetic nanoparticles. They are widely used in engineering, have promising fields of application in medicine, and their use to develop superhigh-density magnetic information storage devices is widely discussed in the literature. The scientific interest in such materials is related to studying the nature of magnetism in objects with sizes no larger than the domain size. Information on progress in studies of magnetic nanoparticles can be found, e.g., in reviews [1–5].

At present, magnetic systems comprising the nanoparticles of magnetite Fe_3O_4 or $MeFe_2O_4$, where Me denotes Mg, Cr, Mn, Fe, Co, or Zn, dispersed in organic or inorganic liquids. The stability of magnetic fluids is ensured by the surfactant coating of magnetic-particle surfaces, which prevents their van der Waals and magnetic dipole–dipole conglutination. The magnetic moment of each nanoparticle at temperatures below the Curie temperature for Fe_3O_4 is close to the total magnetic moment of the contained iron ions. Such a system is a (super)paramagnetic material if the nanoparticle concentration in the medium is low (<5–7%).

The magnetic structure of the Fe_3O_4 single crystals is well known [6]. This compound is a ferromagnet at temperatures below the Curie temperature T_C = 858 K. The Verwey (metal–dielectric) structural transition occurs at the temperature $T_V \approx 123$ K. Magnetite single crystals were also studied in [7–9] using the method of the spin rotation of a polarized positive muon (the so-called μSR method [10]).

The magnetic properties of ferrofluids were analyzed using a number of techniques, including quantum magnetometers (SQUID), Mössbauer spectroscopy [4], and small-angle neutron scattering [11–13].

The magnetic properties of a ferrofluid were studied in [14] using polarized positive muons. The muons resulting from the positive-pion decay $\pi^+ \longrightarrow \mu^+ + \nu_\mu$ are polarized along their momenta due to the parity violation in weak interactions. Hence, the spatial distribution of positrons from the muon decay $\mu^+ \longrightarrow e^+ + \nu_e + \tilde{\nu}_\mu$ is asymmetric with respect to the muon polarization direction. The muon polarization in a medium depends on the interaction of its magnetic moment with the medium, in particular, with the local magnetic fields. Temporal variations in the muon polarization can be

† Deceased.

studied experimentally by observing the time-dependent asymmetry of the $\mu^+ \longrightarrow e^+$ decay.

Water is often used as a medium carrying surfactant-coated nanoparticles. Two μSR signals are typically observed when a muon is stopped in water. One signal is due to the muonium (Mu), a hydrogen-like atom [15, 16] formed by a muon and an electron (μ^+e^-). The muonium magnetic moment precesses in a magnetic field with the Larmor frequency Ω determined by the total magnetic moment of the electron and muon. Another signal is attributed to the positive muon in the diamagnetic state. In the case of water, the muon is most probably located in a water molecule and substitutes one hydrogen atom (MuOH). A muon in a diamagnetic molecule behaves as a free particle. Its spin precesses in a magnetic field with the frequency ω determined by the muon magnetic moment. The ratio Ω/ω of the precession frequencies is 103.

In this paper, the temperature dependences of the polarization, relaxation rate, and precession frequencies of muons in a magnetic fluid based on Fe_3O_4 and heavy water D_2O are studied in the case of "strong" transverse magnetic fields in which the muonium component is not observed because of the high precession frequency and the limited instrumental resolution. The results of studying the muonium component of the muon polarization in "weak" magnetic fields are presented in [17].

EXPERIMENT

The experiments were performed on a beam of longitudinally polarized positive muons from the synchrocyclotron of the Petersburg Nuclear Physics Institute (Russian Academy of Sciences). The degree of muon-beam polarization was about 90%. The measurements were carried out at the μSR facility [18]. The sample was located in a magnetic field transverse with respect to the muon-spin orientation. The transverse magnetic field with a nonuniformity not exceeding 10^{-4} in the central 200-cm^3 part of the magnetic system was generated by the Helmholtz coils. The level of external diffuse magnetic fields was reduced to ~0.05 G by additional solenoids. The samples were cryostat cooled by liquid-helium vapor. The sample temperature was maintained with an accuracy of ~0.1 K.

The studied ferrofluid (Fe_3O_4/2DBS/D_2O) was a solution of nanodispersed magnetite (Fe_3O_4) in heavy water (D_2O) stabilized by the dodecylbenzenesulfonic acid (2DBS). The volumetric concentration of magnetic particles was 4.7%. A milliliter of the ferrofluid contained 0.244-g magnetite, and the ratio of the surfactant and magnetite was 0.3 g of the surfactant per 1 g of Fe_3O_4.

The ferrofluid was placed into a cylindrical copper cell 80 mm in diameter and 10 mm in height. The total thickness of the cell walls along the muon beam was 100 μm. The cylinder axis was parallel to the muon-beam axis. The external magnetic field was perpendicular to the cylinder axis. The column density of the studied material in the beam direction was about 1.2 g/cm^2. The measurements were carried out at temperatures 26–300 K.

The time between the stopping of muons in the sample and the appearance of the decay positrons was measured with a "time–code" converter with a direct conversion range of 10 μs and a channel width of 5 ns. The acquisition rate of useful events in the temporal histogram was about 200 s^{-1}. Each histogram comprised about 2×10^6 events.

The experimental data were fitted with the function

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

where $N(0)$ is the normalizing factor; $\tau_\mu = 2.197$ μs is the positive muon lifetime; P_0, λ, ω, and φ are the initial muon polarization, relaxation rate, and precession frequency and phase, respectively; B is the background; and $b \sim 1$ is the constant dependent on the measurement-facility parameters.

The amplitude of the muon-spin precession in the samples was compared with the precession amplitude in a copper sample for which the coefficient of the asymmetry of positrons from the muon decay was $a = b(P_0/3) = 0.302 \pm 0.002$ in a transverse magnetic field of 280 G.

RESULTS AND DISCUSSION

The parameters P_0, λ, ω, and φ characterizing the behavior of the muon polarization in a medium were found by the least-square fitting of the experimental data with function (1).

Figure 1 shows the measured temperature dependences of the ratio P_0/P_0(Cu) of the initial polarization to the polarization in the reference Cu sample and the relaxation rate λ for the muon (diamagnetic) fraction in a Fe_3O_4/2DBS/D_2O sample for a magnetic field of 280 G. Similar data for a D_2O sample are plotted for comparison. These data on P_0/P_0(Cu) for heavy water do not contradict the results of more detailed measurements [19] in which an increase in the muon contribution was observed with an increase in temperature in the range 100–150 K and in the ice–liquid transition. Our results on the muon-spin relaxation for the diamagnetic fraction in D_2O agree within the measurement accuracy with the results for carefully purified heavy water [19].

The contribution from the muon polarization component for the Fe_3O_4/2DBS/D_2O sample (closed circles in Fig. 1a) is about 30% less than that for D_2O (open

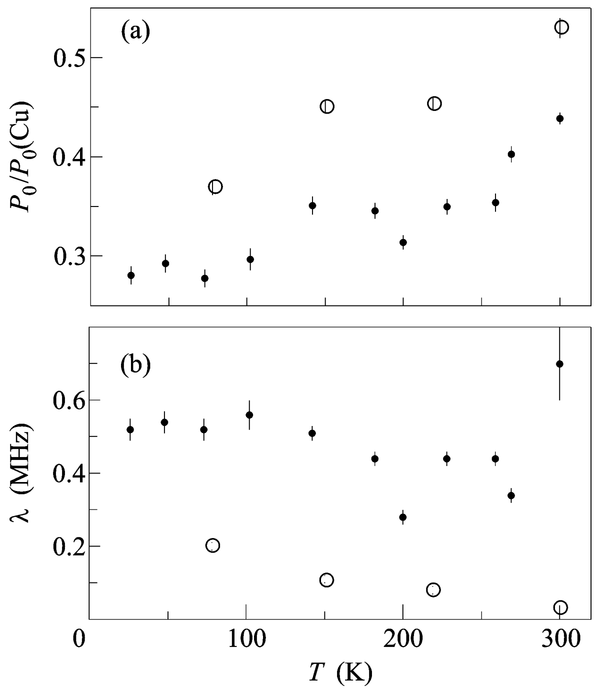

Fig. 1. Temperature dependences of (a) the degree of muon-component asymmetry and (b) the relaxation rate in (open circles) D_2O and (closed circles) Fe_3O_4/2DBS/D_2O in an external magnetic field of 280 G.

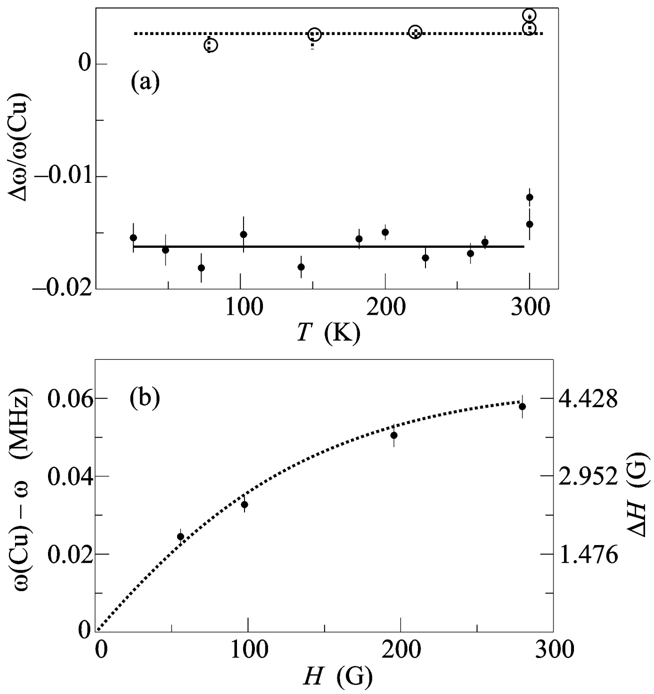

Fig. 2. Shift of the muon-spin precession frequency versus (a) the temperature for H = 280 G and (b) the external magnetic field for T = 200 K. The closed and open circles are the data for Fe_3O_4/2DBS/D_2O and D_2O, respectively. The samples were cooled in the magnetic field.

circles), because muons stopped inside the magnetic nanoparticles in the Fe_3O_4/2DBS/D_2O sample are situated in a higher magnetic field and have a higher precession frequency in comparison with muons stopped outside the nanoparticles. Correspondingly, the diamagnetic polarization component observed in a "strong" magnetic field is attributed to muons stopped outside a magnetic nanoparticle. The fraction of muons stopped in nanoparticles can be up to ~20–25% since the mean column density of Fe_3O_4 along the muon-beam momentum is ~0.25 g/cm^2 for a total sample column density of ~1.2 g/cm^2. The temperature dependence of the muon fraction for the Fe_3O_4/2DBS/D_2O sample (the closed circles in Fig. 1a) is analogous to the above-described temperature dependence of the asymmetry for D_2O. An increase in the muon-fraction contribution typical of D_2O is observed for 100–150 K and for the solid–liquid transition at 3.82°C. A fairly complex temperature dependence for both the asymmetry and relaxation rate for the muon spin were observed in [14] near the water–ice phase transition in the absence of a magnetic field.

The muon-spin relaxation rate in the Fe_3C_4/2DBS/D_2O sample is much higher than that in D_2O. The temperature dependence of the muon-spin relaxation rate exhibits some as yet unexplained features at temperatures above 200 K. However, it is clear that the observed relaxation of the muon spin in the diamagnetic polarization component is caused almost exclusively by the muon-spin interaction with the nanoparticle magnetic moments.

The nanoparticle magnetic moments in the absence of a magnetic field are randomly oriented and fluctuate, so that an external magnetic field gives rise to only a small polarization of the nanoparticle magnetic moments in the sample. As a result, the magnetic field in the medium is different from the external field, so that the (super)paramagnetic muon-spin precession frequency shift should be observed.

The shift $\Delta\omega = \omega - \omega(Cu)$ of the muon-spin precession frequency with respect to the precession frequency in Cu, measured in D_2O and Fe_3O_4/2DBS/D_2O at various temperatures, is presented in Fig. 2a. The samples were cooled in the magnetic field. As seen, the frequency shift is almost temperature independent in both samples. The frequency shift for the Fe_3O_4/2DBS/D_2O sample is about six times larger than that for heavy water and has the opposite sign. This effect is explained by the fact that heavy water is a diamagnet, while Fe_3O_4/2DBS/D_2O is a (super)paramagnet.

The shift of the muon-spin precession frequency is plotted in Fig. 2b as a function of the external magnetic field in Fe_3O_4/2DBS/D_2O. The left- and right-hand vertical axes in the plot correspond to the frequency shift in megahertz and the mean magnetic field generated by the nanoparticle magnetic moments in the medium, respectively. The shift of the muon-spin precession frequency $\Delta\omega = \gamma\Delta B \sim M$, where $\gamma = 13.5544$ kHz/G is the gyromagnetic ratio for the muon, is proportional to the mean magnetic field ΔB generated by the nanoparticle magnetic moments. In turn, the latter field is proportional to the sample magnetization M. It is found experimentally that, similar to paramagnets, the magnetization of samples with low nanoparticle concentrations (less than 6–7%) is described well by the Langevin function (see, e.g., [1])

$$M = nm(\coth\xi - 1/\xi). \quad (2)$$

Here, n is the number of nanoparticles per unit volume, m is the magnetic moment of a nanoparticle in joule/tesla, $\xi = \mu_0 mH/kT$, μ_0 is the magnetic constant, H is the magnetic field strength in ampere/meter, k is the Boltzmann constant in joule/kelvin, and T is the temperature in kelvin.

Our experimental data on the frequency shift were fitted with the function

$$\omega(\mathrm{Cu}) - \omega = \mathrm{const}\, M = \mathrm{const}(\coth\xi - 1/\xi). \quad (3)$$

The fit yielded $\xi = 2.13 \times 10^{-4}H$. The relation $\xi = \mu_0 mH/kT = 2.13 \times 10^{-4}H$ with $\mu_0 = 4\pi \times 10^{-7}$, $k = 1.38 \times 10^{-23}$ J/K, and $T = 200$ K readily yields the mean magnetic moment of the nanoparticles:

$$m = \left(\frac{\xi}{H}\right)\left(\frac{kT}{\mu_0}\right) = 4.68 \times 10^{-19}\ \mathrm{J/T} = 5 \times 10^4 \mu_B. \quad (4)$$

Since the magnetic moment of a Fe_3O_4 molecule is $4.1\mu_B$ [20], the resulting value of m implies that a nanoparticle contains $\sim 1.2 \times 10^4$ Fe_3O_4 molecules and, correspondingly, the nanoparticle size is 12 nm. The latter is in good agreement with a mean nanoparticle size of 11.2 nm derived by fitting the magnetization curves with the Langevin function [21] for the studied sample.

CONCLUSIONS

The relaxation and shift of the precession frequency of the spin of a positive muon in the D_2O medium, where Fe_3O_4 magnetic nanoparticles are randomly distributed, have been studied in a wide temperature range. The mean magnetic field generated by the magnetic moments of nanoparticles randomly distributed in the medium is determined experimentally. It is shown that the mean-field dependence on the external magnetic field does not contradict the Langevin law. The mean size and magnetic moment of the nanoparticles are estimated.

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