Study of the ferrofluid with nanoparticles by the μSR-technique

Material

Magnetic features

Preliminary results

Plans and directions of of the investigation

Material

Ferrofluids are colloidal suspensions of single-domain magnetic nanoparticles in a carrier liquid medium. The magnetic particles are coated with a molecular layer of a dispersant compatible with both the carrier liquid and the magnetic particles. Ferrofluids are usually described as magnetically soft materials, because the magnetization vector follows the applied field without hysteresis.

The compound

Magnetic material

(and not only it)

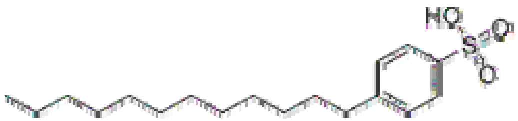
+

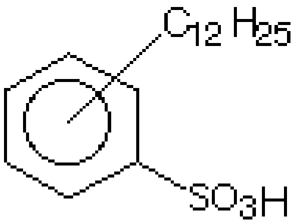
Dodecyl benzenesulphonic acid

+

Solvent

(water, , …)





The compound

Dodecyl benzenesulphonic acid

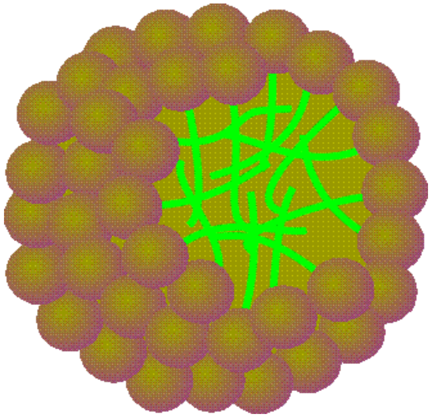
Molecular Mass 326 g/mol
Physical Characteristics
Viscous brownish liquid,

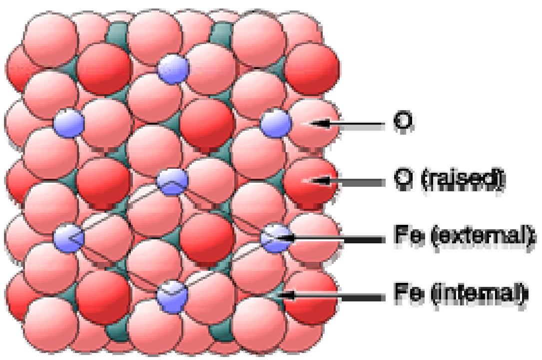
mp: 10^{o}C, bp: 315^{o}C.

Soluble in water, alcohol, ether.

Current Uses Antistatic agent, emulsifier.

Applications General use.





Magnetic features

An externally applied magnetic field induces ordering of the magnetic moments of the particles, giving rise to magnetization of the sample as a whole on a macroscopic scale.

In dilute ferrocolloids the energy of interparticle dipole-dipole interactions is small compared with the heat energy.

Under the effect of an external magnetic field the ferrofluid structure is rearranged. When the concentration of the solid component is sufficiently high and the intensity of the magnetic field is strong enough to stimulate formation of chain clusters.

The game of the magnetism, the viscosity and the gravitation

Viktor Duginov, Repino, 2006

Magnetic features

Usually in a ferrofluid there are two mechanisms of magnetization: the Brown and N´eel ones in force.

According to the Brown mechanism [*Blums E, Cebers A and Maiorov M M 1997 Magnetic Fluids*] the magnetic moment is rotated together with the nanoparticle in the carrier liquid under the influence of an external magnetic field H.

Magnetic features

The time of magnetization relaxation according to Brown mechanism depends on the hydrodynamic volume V , temperature T , and dynamic viscosity η, of the carrier liquid and can be expressed as presented, where the hydrodynamic volume of a particle V is much greater than the magnetic core.

$$\tau_{\mathrm{B}} = \frac{3V\eta}{k_{\mathrm{B}}T},$$

Magnetic features

The Brown mechanism of magnetization of superparamagnetic particles can be blocked by decreasing the temperature of the ferrofluid till the carrier liquid is frozen, and then magnetization of ferrofluid can take place only according to the N´eel mechanism.

Magnetic features

According to the N´eel mechanism the magnetic moment can rotate inside a nanoparticle. An energy barrier must be overcome for this rotation to happen. The height of this barrier is equal to K_1v, where K_1 is the magnetocrystalline anisotropy constant (for magnetite particles $K_1 = 11\ kJm^{-3}$).

The probability of getting over such a barrier is proportional to $\exp(K_1v/k_BT)$.

Magnetic features

According to the N´eel theory the relaxation time is (Eq.) where

$\tau_0 \approx 1$ ns

In practice, in a ferrofluid the two mechanisms can take place simultaneously, and then the effective relaxation time of magnetization is τ_{eff}

$$\tau_{\mathrm{N}} = \tau_0 \exp\left(\frac{K_1 v}{k_{\mathrm{B}} T}\right),$$

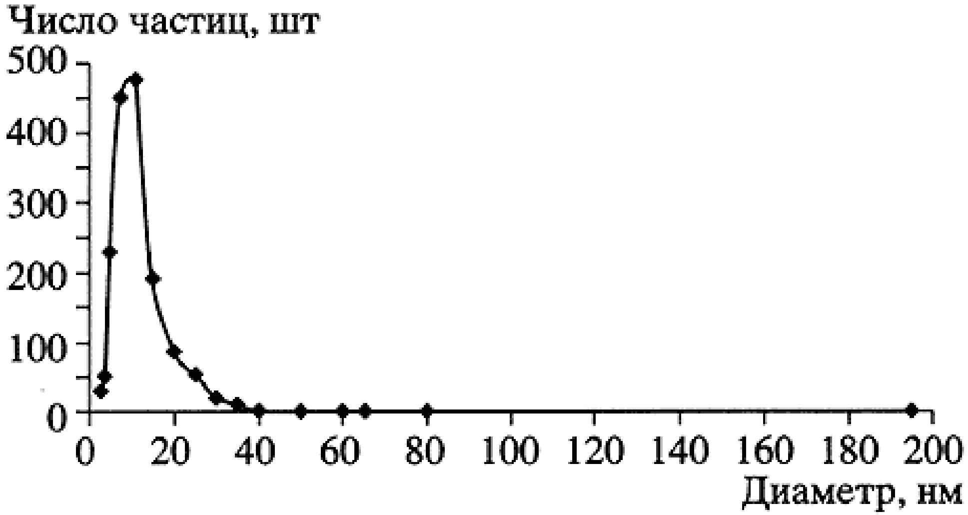
$$\tau_{\mathrm{eff}} = \frac{\tau_{\mathrm{B}} \tau_{\mathrm{N}}}{\tau_{\mathrm{B}} + \tau_{\mathrm{N}}}$$

Magnetic features

As follows from equations, the mechanisms depend on the size of the nanoparticles. In a given ferrofluid the magnetization mechanism whose relaxation time is shorter dominates.

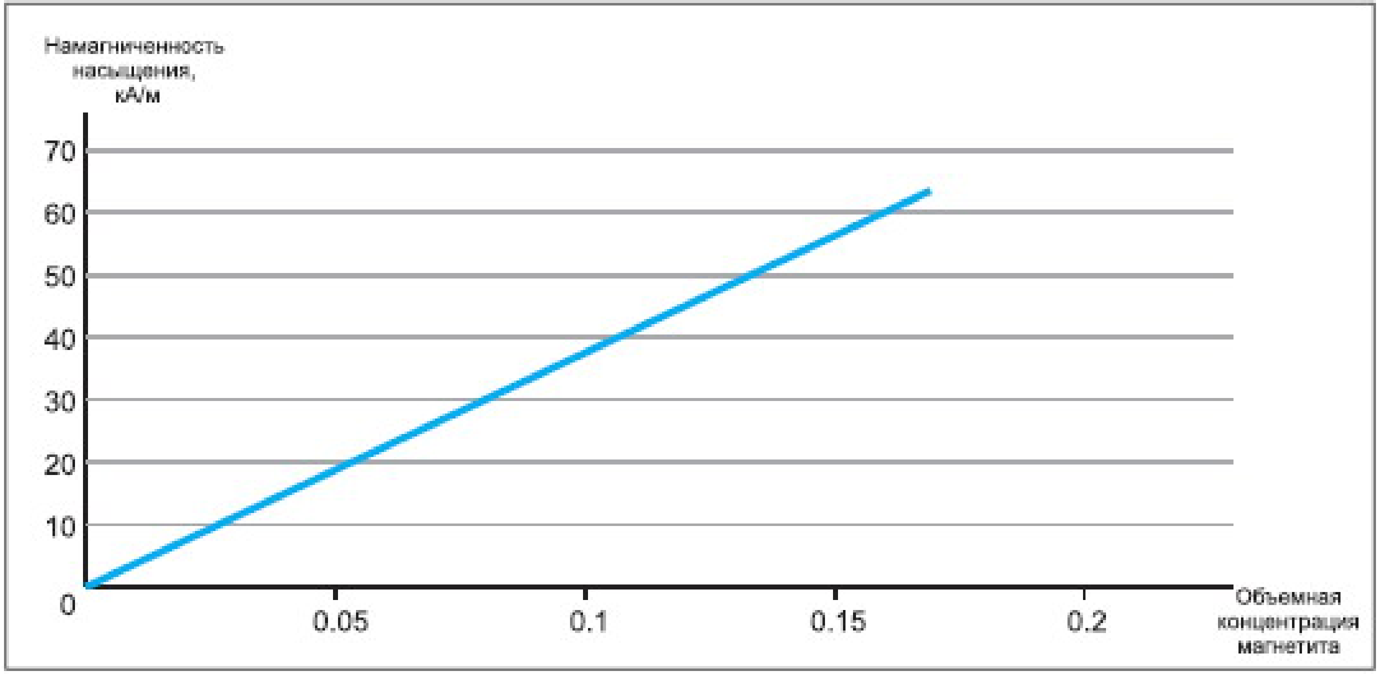
In a polydispersive ferrofluid the N´eel mechanism can dominate for some nanoparticles of size below a certain value, while for the others the Brown mechanism can be dominant.

Cluster diameter distribution



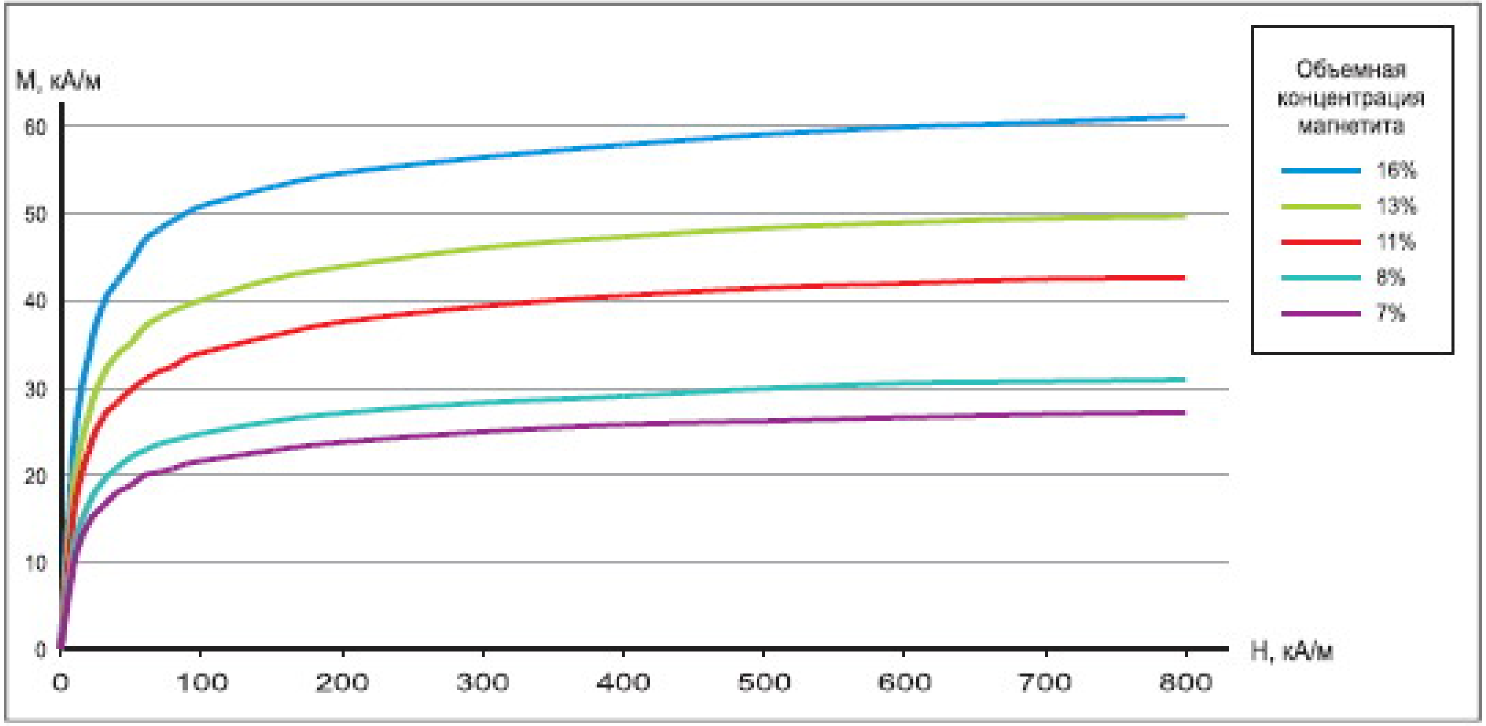
Magnetic features

- magnetic saturation vs concentration

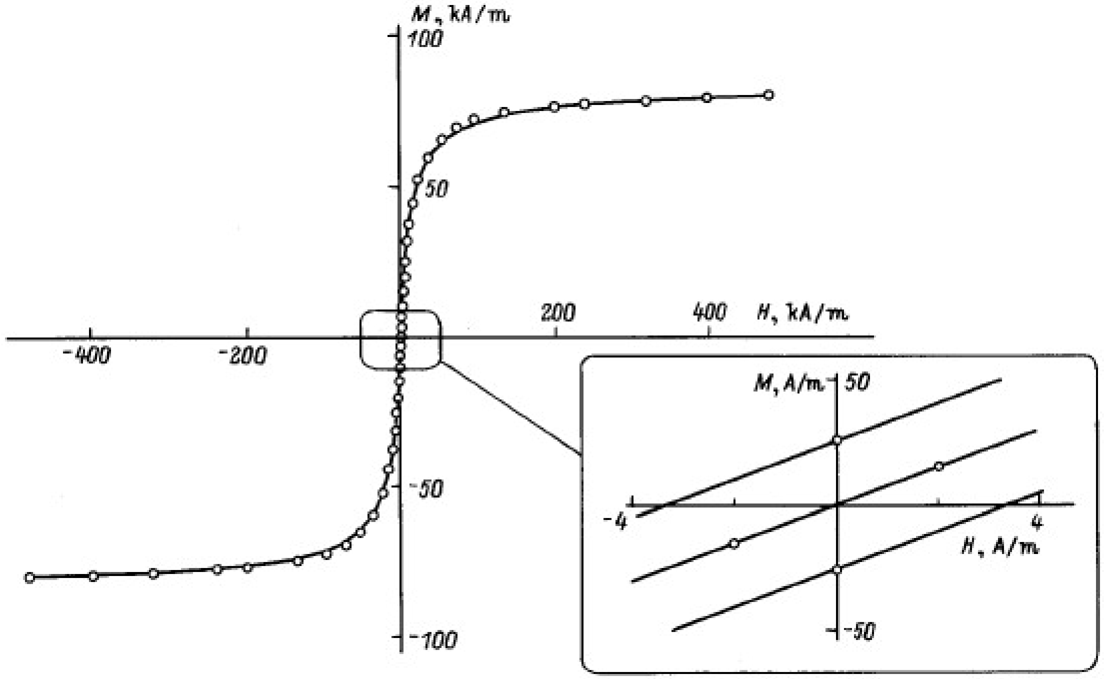


Magnetic features

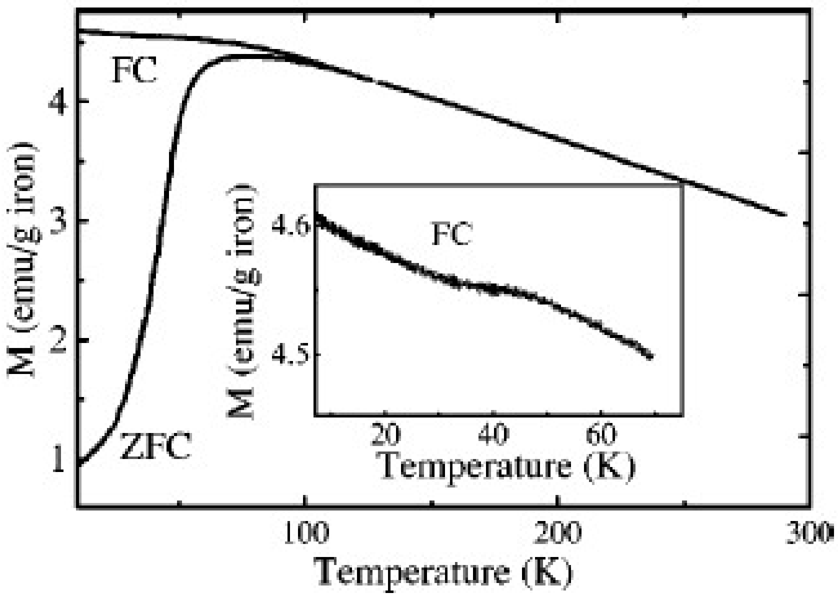
- magnetization vs concentration



Magnetic features

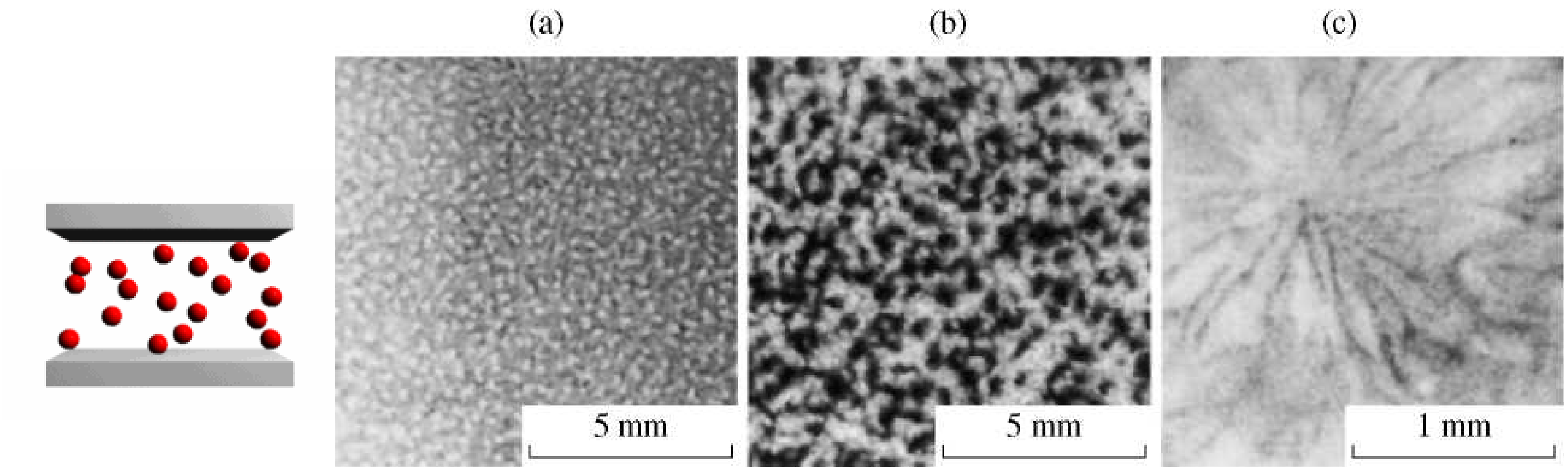


Magnetic features
- possible surface spin-glass transition

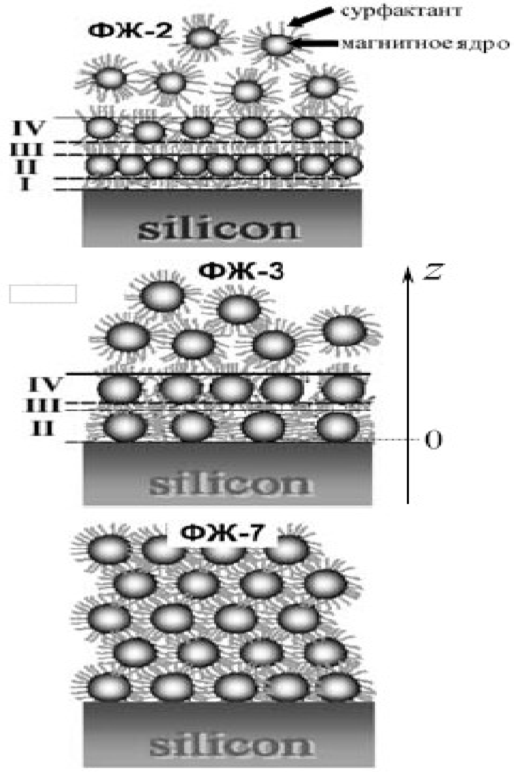


Magnetic features
- ordering in the electric field

(EP = 100 (a), 300 (b) and 1000 kV/m (c))



Magnetic features - separation



$Fe3O4 = Fe^{3+} (Fe^{2.5+})_2O_4$

- 120 K – transition «metal - insulator»
- E.J.W. Vervey - Nature **144**, 327(1939) – ordering Fe^{+3} and Fe^{+2} in different B-positions
- P.W.Andeson – CDW….

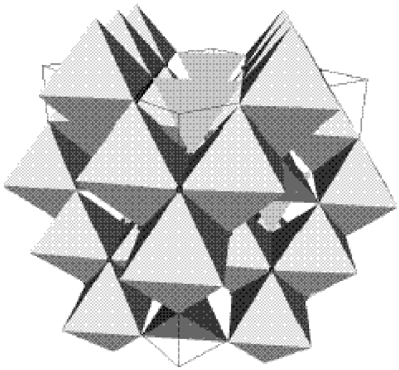
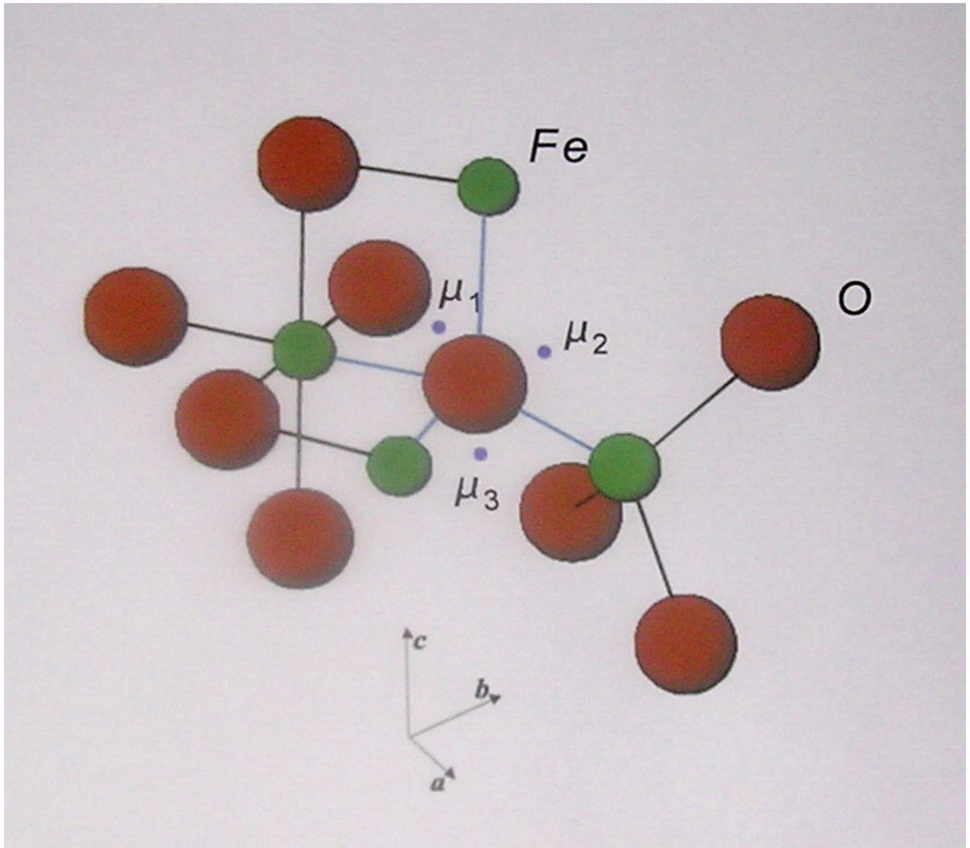
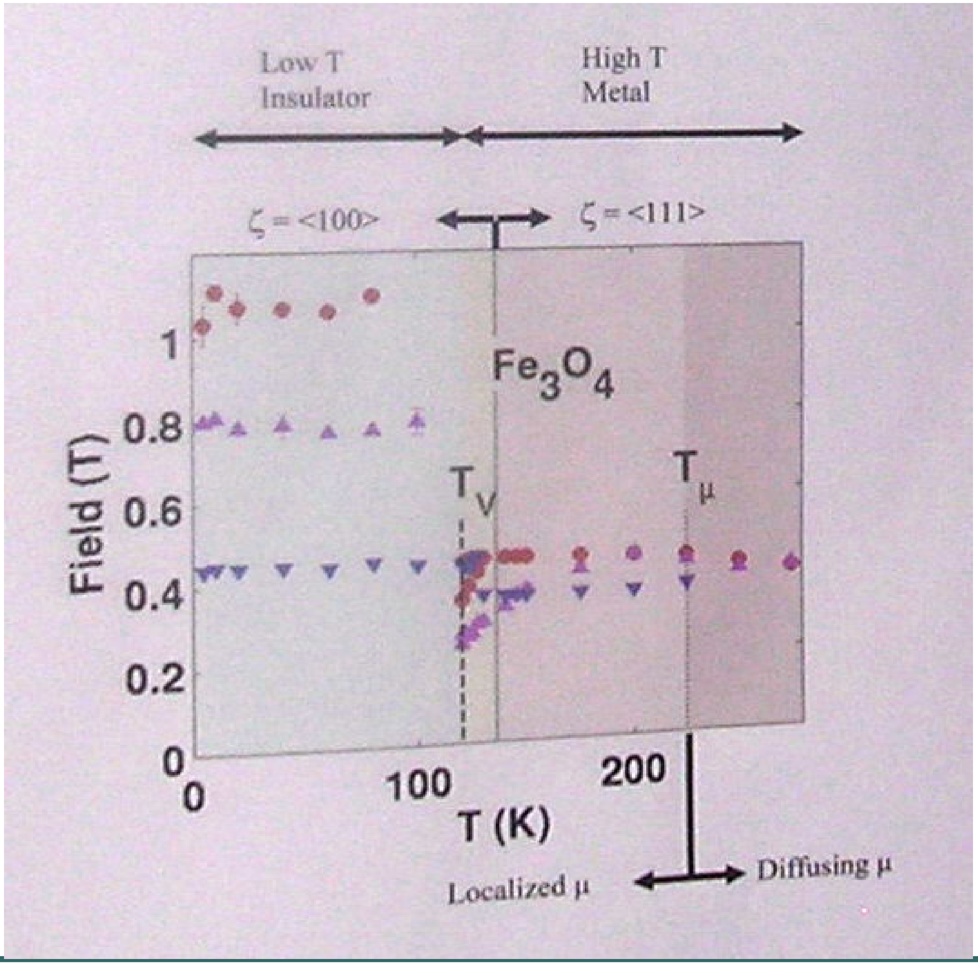


Figure 1: Three-dimensional view of the spinel crystal structure. The *A*-site cations are bonded with four anions, forming isolated tetrahedral. The *B*-site cations are bonded with six anions, forming chains of edge-sharing octahedra. The prototypical spinel is MgAl2O4, a well-known red gemstone with a cubic crystal structure.

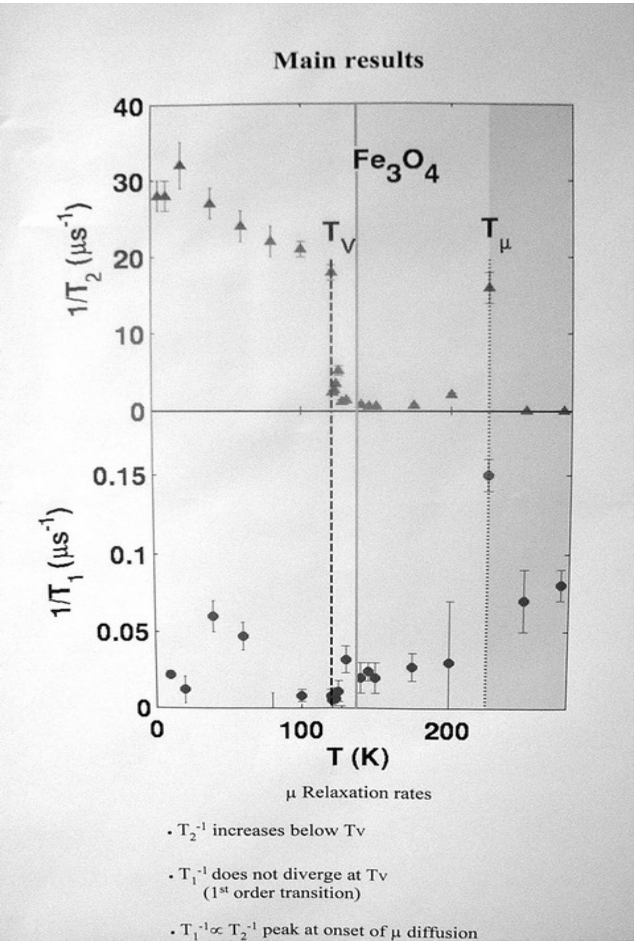
M.Bimbi et al, μSR-2005
(1.1 A от кислорода)



M.Bimbi et al, μSR-2005



M.Bimbi et al, μSR-2005



C.Boekema et al., Phys. Rev. B, 33, 1986

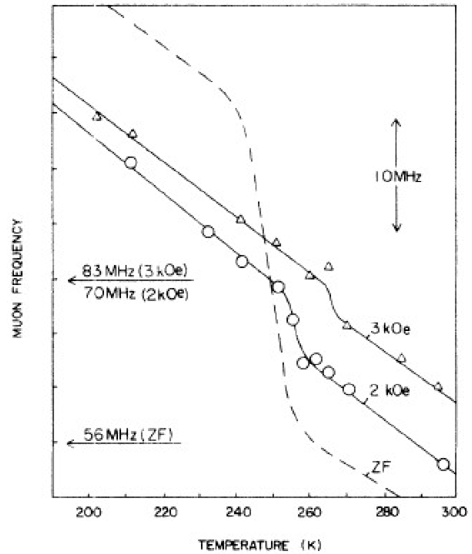


FIG. 1. Temperature dependence of the muon hyperfine frequencies at 0 kOe (dashed line), 2 kOe (○), and 3 kOe (△). Note the temperature shift in the frequency jump. The frequency zeros have been shifted for easy comparison purposes. The frequency division is 0.5 MHz with the actual frequency value indicated at one point for each field. When one plots the local internal field [thus corrected for the effective (Ref. 11) external field] the three lines coincide at higher temperatures. For $B_{ext}=2$ (3) kOe the typical error bar is 0.15 (0.25) MHz.

C.Boekema et al., Phys. Rev. B, 33, 1986

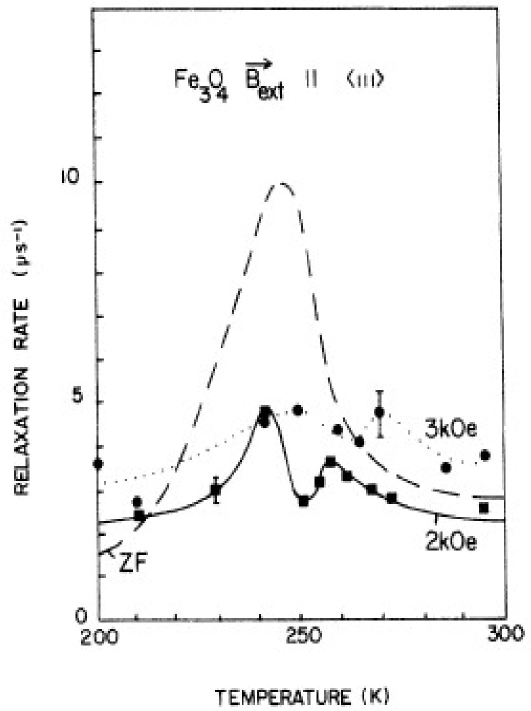


FIG. 2. Temperature dependence of the muon relaxation rate at 0-, 2-, and 3-kOe applied fields. For $B_{ext} = 2$ (3) kOe the errors are 0.3 (0.4) μs^{-1}. The curves are meant to guide the eye. The curve for zero field is taken from Ref. 11.

Water

$$\mu^+ + e^- \rightarrow Mu$$

$$\mu^+ + H_2O \rightarrow MuH_2O^+$$

$$MuH_2O^+ + H_2O \rightarrow MuOH + H_3O^+$$

$$Mu + e_{aq}^- \rightarrow MuH + OH^-$$

$$Mu + e_{aq}^- \rightarrow \text{spin depolarized } Mu$$

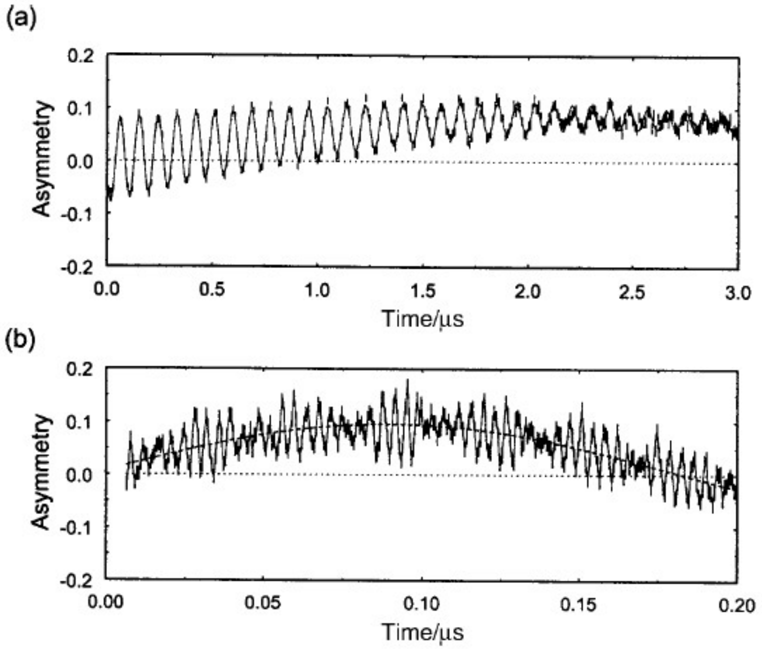
Water

a) 194 G

b) 8 G

$P_{Mu} \approx 0.2$

$P_{Mu} \approx 0.6$



First intention - E-MRS Spring Meeting 2002
June 18 - 21, 2002

Ferrofluids: new opportunities for μSR investigations

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M. Balasoiu* , V. Duginov, FLNP, Dubna, Russia,
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Ferrofluids, ultra stable colloidal suspensions of ferro- and ferromagnetic particles in various carrier liquids, renewed magnetohydrodynamics and extended modern technology with a new dimension. New technologies and devices have their origin in various basic phenomena related to ferrofluids. Every year, there are a big number of new applications in technology, in medicine, in biology. The properties of magnetic colloids are briefly reviewed, with the aim to provide interesting new fields of application of muSR techniques.

Goal

Study the possibility of the application of muonic technique for:

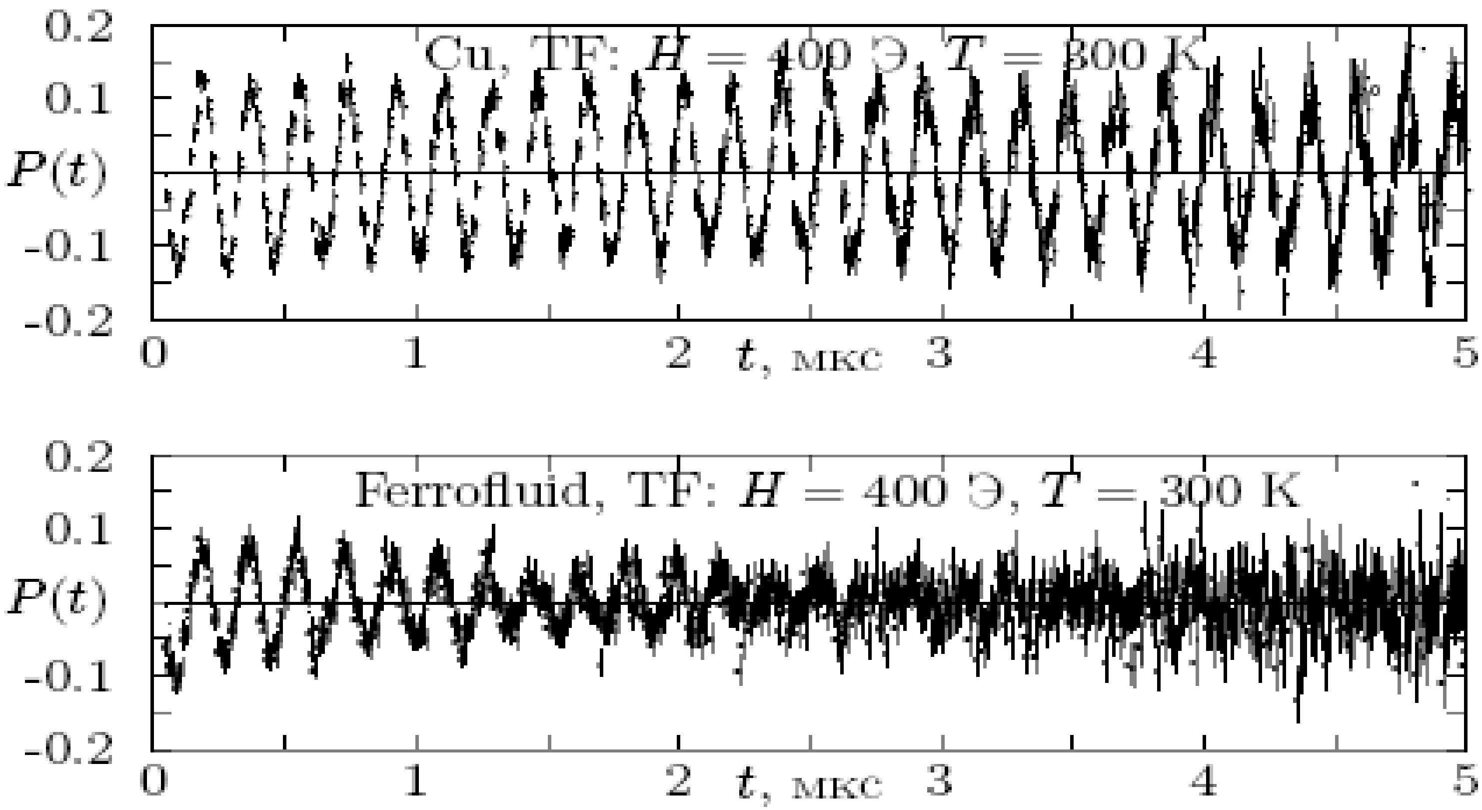
Measurement of the magnetic field inside the nanoclasters

Study of the dynamical behavior of magnetism in nanoparticles

Investigation of the features of the magnetic fluids with different “cores” (Me-Fe2O4, Me - Mg, Zn, Co, …)

Main problem – the difficulty of the extraction of the muSR signal from the clasters

Preliminary experiments at PSI

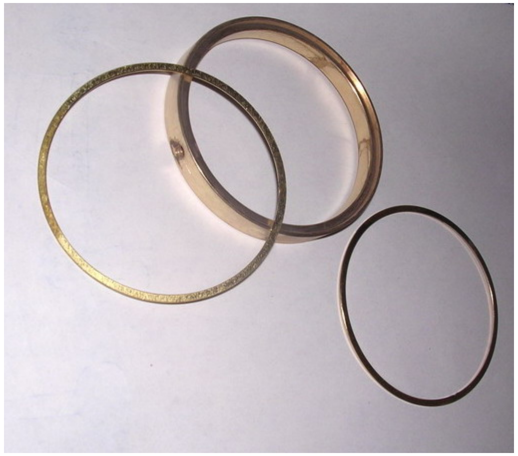


Preliminary experiments at PSI

- The increase of the magnetic field from 100 to 700 G leads the increase of the relaxation rate from 0,3 to 0,8 μs^{-1}
- Frequency shift – superparamagnetism?

Experiments in Dubna

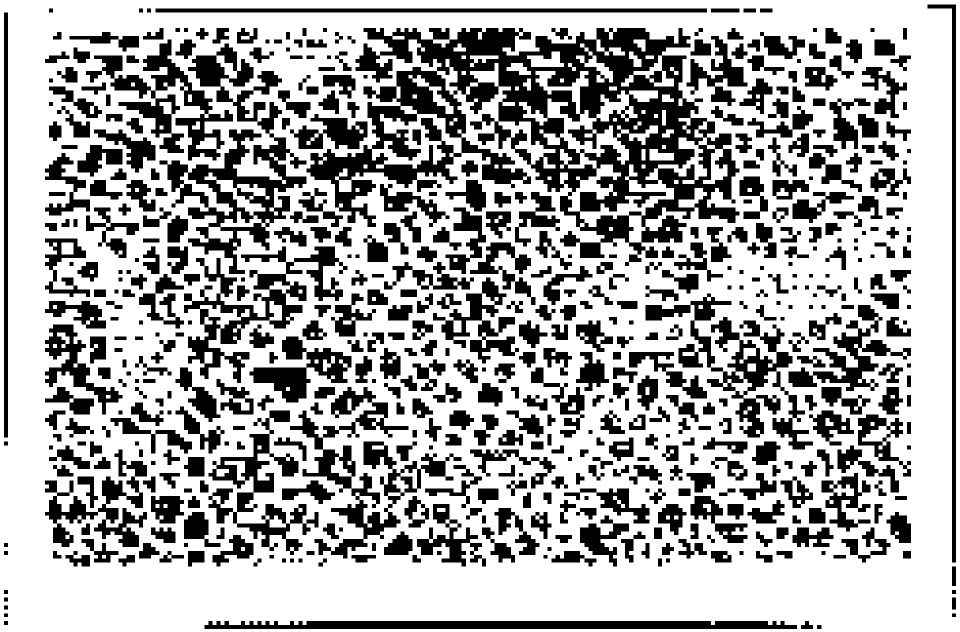
Container for the sample



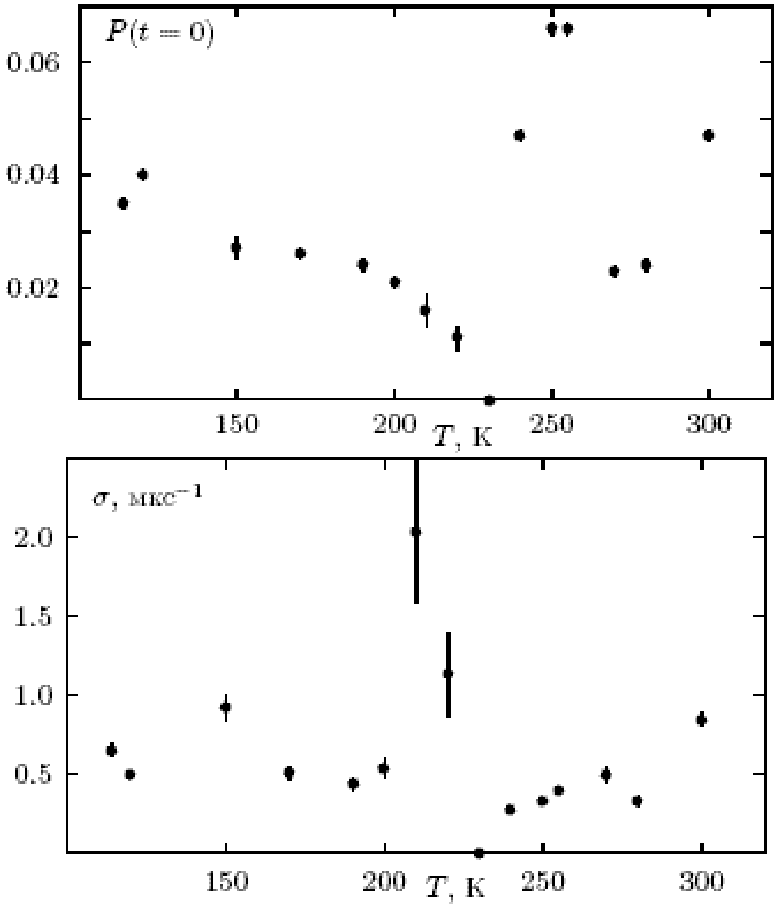
Our sample

- Fe3O4 in deutereited water, stabilized by the DBS surfactant C_v=4.7%.
- Mean diameter of particles d = 118.9 Å with σ = 6.7 Å
- Mean diameter of Fe3O4 “core” d = 50 Å
- 0.244g Fe3O4 in 1 ml ferrofluid;
- 3 g surfactant on 10 г Fe3O4

Sample structure



Dubna experiment
ZF, ΔB~40 Гс при <B>=0



Viktor Duginov, Repino, 2006

Proposed initial experiments

- Background measurements with sample without magnetite
- TF experiments at 10-200 К (400 G)
- Study of the $F_{\mu}=f(H)$
- ZF experiments at $T< T_V$
- «Residual magnetization» - test