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# Magnetically coupled clusters in aggregated maghemite ferrofluid: Mössbauer and magnetization study

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**Abstract** Mössbauer spectroscopy in a weak static magnetic field and measurements of isothermal magnetization loops were used to study the effect of polymer coating of the $\gamma$-$Fe_2O_3$ nanoparticles on the magnetic properties of concentrated ensembles of such nanoparticles. It was found that the individual coating of the nanoparticles by a $\sim$ 1 nm layer of the polymer leads to the observable changes in the shapes of the Mössbauer spectra and the magnetization curves of the ensembles. Modeling of the experimental magnetization curves in the classical Langevin model and analysis of the Mössbauer spectra in the generalized multi-level relaxation model revealed that the establishment of interparticle magnetic dipole interactions leads to both a $\sim$ 30 % increase in the magnetic anisotropy constant and a $\sim$ 35 % increase in the width of the hysteresis loop.

**Keywords** Mössbauer spectroscopy · Magnetization · Superparamagnetic nanoparticles · Dipole magnetic interaction

## 1 Introduction

Composites of magnetic nanoparticles are used today not only in traditional technical areas such as magnetic storage devices [1] or compact permanent magnets [2], but also in biomedicine for creating as an example, biodegradable magnetic beads for targeted magnetic drug delivery [3], or for magnetic hyperthermia treatment of tumor cells [4]. Ferrofluid

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is often used as a starting material for the creation of such devices. This makes it possible to use in the industrial production of these devices a multilayered jet printing. However, the use of such "additive" 3D technologies for magnetic ferrofluids requires further investigation due to the strong dependence of the properties of the resulting composite magnetic material on the particular method of manufacture. For example, in [5] the possibility of creating the magnetic nanocomposite by 2D printing of ferrofluid with two types of inkjet printer heads was investigated. The ferrofluid ink containing magnetite nanoparticles was prepared by adding a dispersion of magnetite nanopowder in n-hexane to insulating ink. The inks were then ejected at room temperature onto standard paper by means of either a thermal ink jet head or a piezoelectric ink jet head. It was found that the prints display a different magnetic behavior. This result, according to the authors, is associated with a different "degree of aggregation" of magnetite NPs in the samples of printed magnets. The possibility of creating 2D magnetic nanocomposites by the formation of a Langmuir monolayer of the oleic acid-coated $Fe_3O_4$ nanoparticles, mixed with stearic acid molecules, at the air/water interface was investigated in [6]. It was found that an increase of a surface pressure in the manufacturing process results in a transition from monolayer of nanoparticles with a strong domain structure to homogeneous continuous monolayer.

The method of multilayer printing can be considered as an example of a method of assembly of such 2D films into a 3D device. In [7] Langmuir-Blodgett films of monodisperse iron oxide nanoparticles have been successfully deposited onto patterned poly(dimethylsiloxane) surfaces. These patterned films of iron oxide nanoparticles were transferred onto solid substrates using micro contact printing. However, the most technologically advanced direct three-dimensional nanoprocessing method is that of two-photon photo polymerization of photopolymers, which provides a novel route for fabricating micro-devices with higher spatial resolution and smaller size [8]. The design and fabrication of remote - controllable micromachines by femtosecond laser induced two - photon polymerization of stable, homogeneous and transparent ferrofluids resin composed of methacrylate groups modified by $Fe_3O_4$ nanoparticles and photoresists were demonstrated in [9]. Micrometer-sized spring and turbine were created for magnetic force remote control. By using an external magnet, both micro-machines could be manipulated to perform the desired task. The combination of photo polymerizable ferrofluid resin and laser processing technology would make a breakthrough in nanotechnology for easy fabrication and remote control of micromachines in a broad range of applications.

Synthesis of 3D micro-devices from polymer-composite materials consisting of magnetic nanoparticles coated with a thin dielectric membrane, requires an understanding of the relationship between the mutual arrangement of the magnetic nanoparticles in the ensemble and the dipole magnetic ordering arising in this structure [10]. "Classic" magnetic materials consist of separate atoms, which have magnetic moments of a few Bohr magnetons and are located at a distance of a few angstroms. The magnetic dipole interaction between such neighboring atoms is too small to lead to the establishment of a magnetic order. Therefore, the magnetically ordered state of "classic" magnetics is determined solely by the exchange interaction. The situation changes radically if individual atoms are replaced by single domain nanoparticles with a size of 10–20 nm, so-called Stoner-Wohlfarth particles [11]. The magnetic moments of such particles, formed by the coherent motion of all spins in the nanoparticle, can reach tens of thousands Bohr magnetons. Therefore, the dipole interaction between neighboring single-domain nanoparticles can exceed the exchange interaction and, as a result, a dipole magnetic order develops in the system [12]. Typically, the aggregation of the dipole-bound clusters of magnetic nanoparticles occurs in the ferrofluid in the process of the gradual displacement of the fluid from the interparticle spacing. This

may lead to the creation of an ordered additive meta-material, which morphology and crystalline structure are different from that of the crystal, grown from the same material, but by the "classical" technology with adding of it's individual atoms [13]. The problem of an experimental study of such systems is that the visualization of an ensemble of magnetic nanoparticles by classical X-ray or electron-microscopic methods is not enough to determine whether the whole ensemble of nanoparticles is magnetically coupled, or the magnetic interactions associated with only a small cluster of nanoparticles inside the ensemble, or all the nanoparticles are connected by electrostatic forces. The problem is complicated by the fact that the magnetic moments of the nanoparticles, involved in the formation of such a cluster, randomly change their directions at nonzero temperature in accordance with the mechanisms of the Neel and Brown relaxation [14]. The Brown relaxation is gradually suppressing with the fluid displacement from the interparticle spacing. Simultaneously the Neel relaxation (consisting for an isolated nanoparticle in the reversal of it's magnetic moment along or against the axis of easy magnetization with the characteristic time of $\sim 10^{-8}$ seconds) becomes more complex. The fact is that, during the formation of a new magnetic meta-material, additional magnetization axes appear in it, affecting the dynamics of the magnetic moments of the individual nanoparticles. After the establishment of a dipole magnetic order one of these axes becomes a new axis of easy magnetization of the meta-material and the Neel relaxation of magnetization vectors of individual nanoparticles is terminated.

This article examines the ability to extract quantitative information about the dipole magnetic ordering in the ensemble of superparamagnetic nanoparticles from Mössbauer spectra of the ensemble, measured at different temperatures in the presence of a magnetic field, and from the Isothermal magnetization loops measured by means of a vibrating sample magnetometer.

## 2 Samples

All samples for the study were made on the basis of the same batch of ferrimagnetic $\gamma$-$Fe_2O_3$ nanoparticles and differ only in the way of their association in the ensembles. First of all an electrostatically stabilized aqueous dispersion of these iron oxide nanoparticles was prepared. Then one portion of the ferrofluid was additionally sterically stabilized in accordance with the procedure based on the RAFT polymerization and described in [15]. As a result the nanoparticles were coated individually with a short poly (acrylic acid) -b-poly (acrylamide) copolymer. The procedure was aimed to reduce the probability of the magnetic interaction between nanoparticles in the ensembles. Thermogravimetric analysis yields the iron oxide content in the dried particles, consistent with dry polymer coating of approximately 1 nm in thickness. Then the samples for investigation were prepared from both the initial electrostatically stabilized ferrofluid and the sterically stabilized ferrofluid. The details of their preparation procedure were reported previously [16]. Preliminary Mössbauer studies [17] have shown that the magnetic beads, prepared from the same nanoparticles by different methods, exhibit different values of the magnetic anisotropy. In this paper to demonstrate the effect of inter-particle interactions, we chose two types of samples having the minimal and maximal magnetic anisotropy.

Samples NP (Nano Particles) for Mössbauer study were prepared by drying of the sterically stabilized ferrofluid, containing $\gamma$-$Fe_2O_3$ nanoparticles, individually coated with a thin layer of polymer.

Samples DI (Dipole-Interacting) were prepared by drying of the initial electrically stabilized ferrofluid, containing $\gamma$-$Fe_2O_3$ nanoparticles without individual polymer coating.

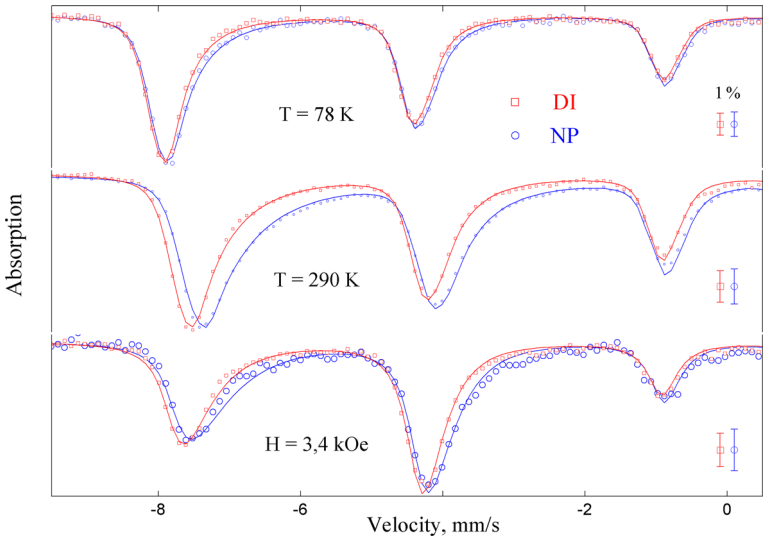


**Fig. 1** The 1, 2 and 3 (*leftmost*) lines of the $^{57}$Fe Mössbauer absorption spectra (markers) measured at 78 and 290 K and in a weak external magnetic field of 3.4 kOe at 290 K for the samples of magnetic beads DI (red) and initial sterically stabilized nanoparticles NP (blue), containing the same magnetic nanoparticles in different environments. All measurements are brought to the same absorption effect for the ease of comparison. Vertical sizes of the markers on the curves indicate experimental errors (doubled standard deviation). Solid lines represent theoretical spectra

## 3 Experimental results

Mössbauer spectra were measured at the temperatures 78 - 290 K with electro-dynamical type spectrometer MS-1104 Em, working in the constant acceleration mode. $^{57}$Co in a rhodium matrix of 5 mCi activity was used as a source of gamma-radiation. The isomer shifts were determined in relation to the absorption line of $\alpha$-Fe. The samples were measured at the temperatures 78, 200 and 290 K and in the presence of a magnetic field of 3.4 kOe at 290 K.

Figure 1 shows the lines 1, 2 and 3 of the Mössbauer spectra of the samples (NP) and (DI). The difference in the spectra observed is due only to the method of packing of the particles in the ensemble. The spectra, measured at high temperature (290 K), are showing the maximal difference. At low temperature (78 K) or in the magnetic field (3,4 kOe) the difference between the spectra decreases, indicating the magnetic relaxation nature of the observed effect, since both a temperature decrease and an external magnetic field switching on should reduce the frequency of fluctuations of the magnetic moment of single-domain nanoparticles. Therefore, it can be stated that all the visible differences in the spectra in Fig. 1 are associated exclusively with the establishment of magnetic - dipole interactions between nanoparticles.

The most prominent feature of the Mössbauer spectra in the ensembles of interacting superparamagnetic nanoparticles, presented in Fig. 1, is a specific asymmetric shape of the spectral lines with sharp outer and extended inner edges [18–23]. This unusual form of lines was originally explained in a theoretical paper [24] where it was developed for the so-called generalized two-level relaxation model based on the classical model of Neel. The basic assumption of the generalized model is that the relaxation between the states of the

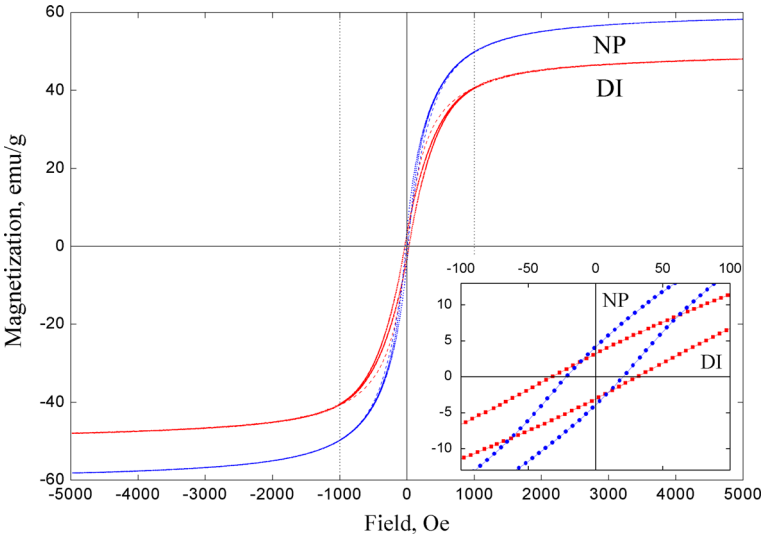


**Fig. 2** Field dependent magnetization measured at 300 K for the samples of magnetic beads DI (red) and base sterically stabilized nanoparticles NP (blue), containing the same magnetic nanoparticles in different environments. Dashed lines represent theoretical curves

nanoparticles with opposite directions of its magnetic moment never occurs as a transition between equal energy levels, since even a weak interaction between neighboring particles must necessarily displace the energy levels. In this paper, for obtaining qualitative and quantitative information about the sizes of magnetically connected clusters within the aggregate of magnetite-based ferrofluid from Mössbauer and magnetization data, a calculation procedure based on the further development of this idea [25] was used.

The magnetization measurements of the samples were performed using the Quantum Design Vibrating Sample Magnetometer with an oscillation frequency 40 Hz. Hysteresis loops were measured at the temperature 300 K with a maximum magnetic field 5 kOe. The step of 5 Oe was used in the range absolute field values less than 1000 Oe and that of 20 Oe was used in the range absolute field values 1000 - 5000 Oe.

Modeling of the magnetization curves of samples NP and DI in strong fields was carried out in the classical Langevin model

$$\sigma = \sigma_s L(x) = \sigma_s (\mathrm{cth}\, x - 1/x), \tag{1}$$

$$x = V\rho\sigma_s H / k_B T, \tag{2}$$

where $\sigma$ is specific magnetization of the sample, $\sigma_s$ is it's value at saturation, $V$ is the volume of the particles, $\rho$ is the density of the material, $H$ is the magnitude of the applied magnetic field, $k_B$ is Boltzmann constant and $T$ is temperature, using the particle size distribution given by Mössbauer spectroscopy. The magnetization curves at room temperature in a strong magnetic field show almost superparamagnetic behavior, however, under careful measurement, demonstrate a little hysteresis loop, as shown in the inset. From the theoretical analysis this central part, restricted by the two vertical dashed lines, is excluded. This restriction is not essential as the main parameter used in the model is the saturation magnetization, determined accurately. The theoretical curves are shown in the Fig. 2 by the dashed lines. The presence of the hysteresis loop in the magnetization curves of the samples, consisting of electrically insulated single domain superparamagnetic nanoparticles, indicates

the establishment of a so-called superferromagnetic state, associated with the presence of the magnetic dipole interaction between the particles. The width of the hysteresis loop $H_c^{hy}$ was 16.0 (2) Oe for the sample NP and 25.3 (1) Oe for the sample DI. Thus, it appears that the interparticle dipole interactions in the sample DI resulted in a $\sim 35$ % increase in the width of the hysteresis loop $H_c^{hy}$ compared to sterically stabilized particles.

## 4 Discussion of results

The model for the joint analysis of the Mössbauer spectra, used in this article is based on a generalization of multi-level relaxation model [26], which takes into account the anisotropy of magnetic nanoparticles, the diffusion of their uniform magnetization and quadrupole hyperfine interaction [27]. This multi-level relaxation model is based on a quantum-mechanical description of the nanoparticles with the total spin $S$ and $2S+1$ possible spin's projections $S_z$ to the easy magnetization axis, so that we have the following expression for the particle energy:

$$E = KV\cos^2\theta = KV\,S_z^2/S^2, \tag{3}$$

where $K$ is the axial magnetic anisotropy constant and $\theta$ is the angle between the magnetization vector and the easy magnetic axis of the particle. The intensity of the random transitions between energy levels is determined by the phenomenological diffusion constant $D$, and the calculation of the Mössbauer spectra in conditions of the quadrupole interaction is carried out in the framework of stochastic approximation.

To describe the Mössbauer spectra in a weak static magnetic field we used recently proposed extension of the standard multi-level relaxation model [25], when the energy of the particles is determined by the expression of more general type:

$$E = KV(\cos^2\theta + 2h\ \cos\Theta), \tag{4}$$

$$h = H/H_c,\quad H_c = 2K/M_0, \tag{5}$$

where $\Theta$ is the angle between the direction of the external field and the magnetic moment of the particle, $H_c$ is the critical field of magnetization reversal, $M_0 = \rho\sigma_s$ is bulk magnetization.

The quantitative analysis of the experimental spectra requires taking into account a variety of particles sizes in the studied samples, for which we chose Gaussian form of particles distribution over their diameters:

$$P(d) \propto \exp(-(d/d_{av} - 1)^2/2\gamma_d^2), \tag{6}$$

where $d_{av}$ is the most probable diameter and $\gamma_d$ nis the relative width of distribution, so the averaged spectrum is expressed as

$$\sigma_{av}(\omega) = \int_0^\infty \sigma(\omega, x)x^3P(x)dx \Big/ \int_0^\infty x^3P(x)dx \tag{7}$$

Here we have taken into account a different number of atoms in the particles with different sizes. This approach allowed us to fulfill consistent analysis of the minimal set of experimental data, including for each sample three of the Mössbauer spectra measured at two different temperatures and in a magnetic field and the magnetization curve, and to determine the most important characteristics of the studied ensembles of particles, e.g. their size distribution.

**Table 1** Characteristics of the ensemble of dipole interacting magnetic nanoparticles DI and the initial sterically stabilized nanoparticles NP, corresponding to their Mössbauer spectra and magnetization curves, shown in Figs. 1 and 2: $\gamma_d$ – the relative width of Gaussian distribution of nanoparticles over their diameters, $d_{av}$ – the average particle diameter, $D$ – diffusion constant, $KV$ – the average energy barrier in the anisotropy field, $H_c^0$ – full magnetization reversal field, $\sigma_s$ – the saturation magnetization. The mean square errors in the last digits are shown in brackets

| T = 290 K | | | T = 78 K | | | T: Both / Sample Both | |
|---|---|---|---|---|---|---|---|
| | | | T = 290 K | T = 290 K | T = 290 K | | |
| $KV$, K | 1340 (10) | 1890 (20) | $KV$, K | 740 (10) | 950 (20) | $\gamma_d$ | 0.192 (3) |
| $H_c^0$, kOe | 1.75 (4) | 1.70 (3) | | | | $d_{av}$, nm | 11.5 (4) |
| $\sigma_s$, emu/g | 60 (3) | 50 (3) | | | | $D$, kHz | 29 (2) |

Table 1 summarizes the main characteristics of both the ensemble of dipole interacting magnetic nanoparticles DI and the initial sterically stabilized nanoparticles NP, associated with their Mössbauer spectra and magnetization curves, shown in Figs. 1 and 2. These parameters were obtained by joint analysis of the entire group of three Mössbauer spectra and the magnetization curve in the framework of the approach, described above. This procedure assumes that the isomer shift $\delta$, quadrupole splitting $q$, the diffusion constant $D$ and the relative width of the Gaussian distribution of nanoparticles over their diameters $\gamma_d$ for both samples are the same, because they are composed of the same particles. The last parameter is proved to be close to 0.2, which indicates a good monodispersity of the initial particles.

The average particle diameter $d_{av}$ was found in two ways: directly from the analysis of shapes of the magnetization curves as well as on the basis of the field of full magnetization reversal $H_c$, determined from the Mössbauer spectra in the magnetic field, taking into account the saturation magnetization $\sigma_s$. Both methods gave similar values close to 11.5 nm for the average diameter of nanoparticles, and so, taking in mind previously found width of their size distribution, we may conclude, that most of the particles have diameters from 9 to 14 nm.

The diffusion constant $D$ characterizes the intensity of the Brownian motion of the vector of the particle's magnetic moment and leads to accelerated decay of the system's electron-nuclear states and so to corresponding broadening of its Mössbauer line. The natural width of the $^{57}$Fe Mössbauer line in terms of the frequency is approximately 1 MHz ($(\tau \sim 10^{-7}\text{s})^{-1}/2\pi$). However, a joint analysis of the high quality experimental spectra within the realistic model of magnetic relaxation allows us to diagnose the dynamic processes in the systems of nanoparticles with an accuracy of about 1 kHz. In our case the analysis revealed the presence of a weak relaxation with a frequency of 29 kHz.

Specified heights of the energy barrier in the anisotropy field $KV$ refers to the particles with average size $d_{av}$. Distribution of the anisotropy barrier $KV$ assumed to be related only to distribution of the particles volume $V = \pi/6 \cdot d^3$, and its temperature differences are considered to be due to the dependence $K(T)$. The values of the anisotropy constant $K$ are of the order 1 – 2 K/nm$^3$ ($\sim 10^{-2}$ J/cm$^3$) in the range 78 – 300 K. It's unusual temperature behavior probably arises from some limitations of a rather simple multilevel model, used for the data processing, whereas recent more accurate theoretical considerations show, that the additional modes of thermal agitations exists for ferrimagnetic particles (in contra to ferromagnets) which energy spectrum greatly exceeds classical anisotropy barrier and effectively leads to its growth with temperature [29]. Nevertheless, we expect that this fact is not so

critical for comparison of measurements obtained at the same temperature and that the variation in the effective energy barrier $KV$ for different samples correctly reflects the influence of the particles environment. For the sample DI the barrier height at room temperature is 1890(20) K and for the sample NP it is 1340(10) K. Taking into account the identity of magnetic nanoparticles in the samples DI and NP we can conclude, that the dipolar interaction in the sample DI leads to nearly 30 % increase of the magnetic anisotropy constant $K$.

Field of complete magnetization reversal $H_c$ is the value of the external field at which an only one minimum remains in the energy profile of all particles. It determines the maximum possible width of the hysteresis loop in the low-temperature limit.

Saturation magnetization $\sigma_s$, found from the field dependence of the magnetization, is the magnetic moment per unit mass of the magnetic nanoparticles in the substance. This value was obtained using weight percentage of the initial particles in the polymer beads provided by the producer. Slight difference in saturation magnetization for two measurements possibly originates from the low accuracy of the weighing because of the strongly limited amount of the studied samples. In the analysis we assumed that the increase of the total momentum in the external field occurs due to the rotation of the magnetic moments of the particles along the field while their magnitudes remain unchanged.

## 5 Conclusion

It was found that the establishment of a magnetic dipole interaction in polymer-composite samples of magnetic nanoparticles leads to changes in the shape of the Mössbauer spectra and magnetization curve in comparison to initial nanoparticles. Both a $\sim$ 30 % increase of the magnetic anisotropy constant and a $\sim$ 35 % increase of the width of the hysteresis loop were detected for the sample DI in comparison with that of the initial sterically stabilized nanoparticles NP. Commensurability of these changes indicates the possibility of the development of metrology techniques for quantitative characterization of the magnitude of interparticle magnetic dipolar interactions in polymer-composite nanomagnets by any of these methods. However the joint processing of data of Mössbauer and magnetic measurements under an adequate general multilevel relaxation model can greatly improve the accuracy of the metrology.

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