

# EFFECT OF POLYDISPERSITY ON THE MAGNETIC PROPERTIES OF ORDERED 2D ARRAYS OF FERRITE NANOPARTICLES

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The construction of novel nanostructured materials attracts much attention in materials research due to possibilities for contributions in low-dimensional research and/or in potential technological applications. In this communication we present the formation of ordered arrays of  $\gamma$ -ferrite nanoparticles (NP) by the Langmuir-Blodgett technology (layer-by-layer deposition) and characterization of the magnetic properties by Mössbauer spectroscopy and vibrational magnetometry. The effect of a non-ideal dispersion of particle size on the phase transition from superparamagnetic to ferromagnetic state of the 2D nanoparticle system is discussed from the viewpoint of potential applications.

**Key words:** ferrite nanoparticles, Langmuir-Blodgett films, polydisperse nanoparticle system, Mössbauer spectroscopy, vibrating sample magnetometer, magnetic properties

## 1 INTRODUCTION

The construction of novel nanostructured materials attracts much attention in materials research due to potential applications in electronics, optics and magnetism. Physical properties of materials are in this case determined only by three parameters: the size of particles, their composition and topology of the system. The choice of technology used for organization of the system is thus important from the point of view of macroscopic properties. For the last several decades, preparation and processing of fine magnetic particles has been motivated by their variety of applications, such as ferrofluids [1, 2], data storage [3, 4], and medicine [5–8]. Major basic scientific interest in small magnetic particles has been focused on studies of the magnetic properties of single-domain magnetic particle assemblies [9]. More recently, with advances in colloidal nanocrystal synthesis, interest has grown in producing nanostructured magnetic thin films with well-defined structures and controlled properties [10].

In this communication we present the formation of ordered arrays of maghemite nanoparticles by means of the Langmuir-Blodgett technology whose property dwells in the capability of depositing a defined number of monolayers (layer-by-layer) at ambient temperature, *ie*, even a monomolecular-layer is possible, and of preparing two-dimensional and quasi three-dimensional magnetic nanoparticles arrays [11]. The magnetic properties of NP system with a non-ideal dispersion of particle sizes are evaluated from point of view of potential applications (*ie*, exploitation at low-cost liquid nitrogen regime).

## 2 THEORETICAL APPROACH

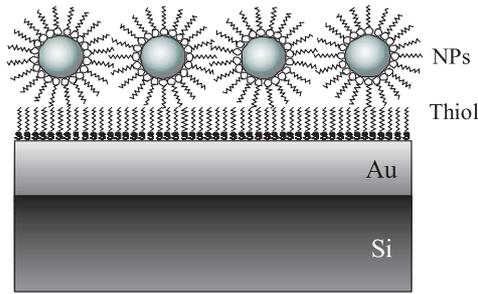
Small magnetic particles above the so-called blocking temperature are in the superparamagnetic state (SPM) and magnetization can relax by the Néel relaxation, a thermal disorder process. It is caused by the reorientation of the magnetization vector inside the magnetic core against an energy barrier [12].

In the SPM state, the direction of the particle magnetic dipole moment thermally fluctuates with a characteristic relaxation time  $\tau$ , determining a period in which the magnetic moment spends in a particular direction [13]. In the absence of a magnetic field and of the interaction effects between the particles, the relaxation time can be expressed by the Arrhenius-Néel formula [14]

$$\tau = \tau_0 \exp\left(+\frac{E_B}{k_B T}\right) \quad (1)$$

where  $E_B$  is the anisotropy energy barrier separating two easy directions of magnetization,  $k_B$  is the Boltzmann constant,  $T$  is temperature,  $\tau_0$  is the temperature and field independent pre-exponential factor which in the case of maghemite NPs is of the order of  $10^{-10}$  s. If  $\tau$  is shorter than a characteristic time of measurement ( $\tau_m$ ), the maghemite nanoparticles exhibit SPM fluctuations of the magnetic moment. When temperature is decreased below the blocking temperature  $T_B$ , the thermal energy becomes smaller than the anisotropy energy barrier and the particle magnetic moment is blocked to a particular direction and the nanoparticle system exhibits ferromagnetic (FM) properties.

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**Fig. 1.** Sketch of prepared NPs multilayer sample. The surface of silicon wafer (Si) with evaporated gold layer (Au) was modified with alkylethiolate layer (Thiol). The Langmuir-Blodgett film of magnetic nanoparticles (NPs) encapsulated into organic envelope was subsequently deposited.

**Table 1.** Survey of fitting parameters of Mössbauer spectra: isomer shift (IS), hyperfine field (HF) and the relative area.

	IS (mm/s)	HF (T)	relative area (%)
Doublet	0.39	-	41
Sextet A	0.33	45.9	24
Sextet B	0.48	39.5	35

According to the Néel-Brown relaxation model for isolated particles, the blocking temperature  $T_B$  can be expressed as

$$T_B = \frac{KV}{k_B \ln(\tau_m f_0)} \quad (2)$$

where  $K$  is the anisotropy constant,  $V$  is the volume of each particle,  $\tau_m$  is the measurement time, and  $f_0$  is the frequency factor. If the size of SPM  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles is comparable or smaller than 15 nm, large differences in their magnetic properties were found [15–17]. For a maghemite nanoparticle in our experiment we chose  $K = 10^5$  J/m<sup>3</sup> [18],  $\tau_m = 100$  s [19] and  $f_0 = 10^{12}$  s<sup>-1</sup> [20] (the relationship is shown in Fig. 2, left).

Recent publications reported on physical properties of two-dimensional close-packed arrays of microscopic uniformity extending to the cm scale, which were formed using the Langmuir-Blodgett (LB) technique [21]. Similar close-packed arrays were recently used for magnetotransport and magneto-optical experiments [22].

### 3 EXPERIMENTAL

Langmuir-Blodgett (LB) technique was used to produce two-dimensional arrays of organically functionalized NPs of  $\gamma$ -ferrite (maghemite) approx. 10–20 nm in diameter encapsulated in an oleic acid envelope [23]. The NPs dissolved in chloroform were added in small quantities onto the water surface. After evaporation of the volatile solvent the particles spontaneously formed a Langmuir monolayer at the air/water interface. For preparation of defect free NP layers it was necessary to hydrophobize the substrate surface. A self-assembled alkylethiolate monomolecular film on the evaporated gold layer was formed for this purpose by immersion into a 1 mM

1-hexadecane thiol in ethanol solution for 24 h at room temperature. Subsequently, it was extracted from the solution and thoroughly washed in chloroform. The transfer of the NP monolayer onto a solid substrate was performed in the LB trough (model 611, NIMA Technology, Coventry, U.K.) by vertical dipping at the surface pressure of 10 mN/m.

### 4 RESULTS AND DISCUSSION

Scanning electron microscopy (SEM) was used for evaluating the NP size distribution (shown in Fig. 2, right). In our case the system of NPs exhibits a wide distribution of particles size corresponding to (according to Eq. 2) different blocking temperatures and hence a co-existence of particles being in the SPM and FM states is expected at a particular temperature. The dashed line in Fig. 2 (right) indicates the size of nanoparticles at the superparamagnetic-ferromagnetic phase transition at liquid nitrogen temperature (LNT) with the NPs in the SPM state located to the left from the boundary (approx. 30%) and the NP in the FM state located to the right.

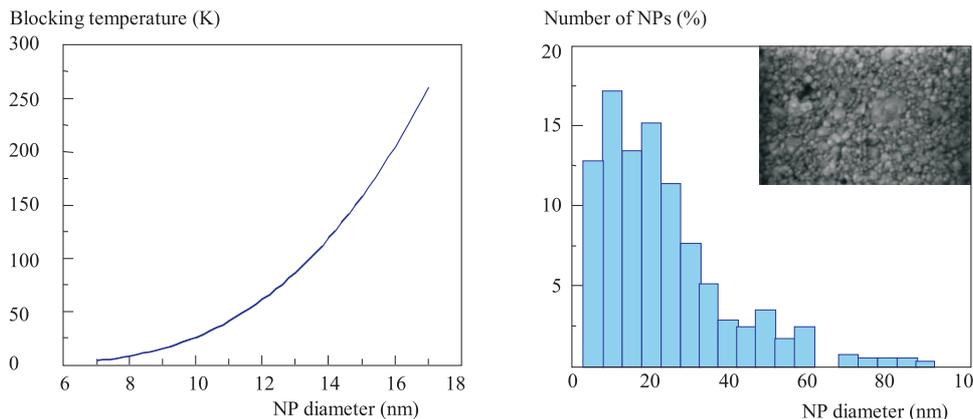
Magnetic characterization of the NPs planar array was carried out using Mössbauer spectroscopy and vibration magnetometry.

The <sup>57</sup>Fe Mössbauer absorption spectra of the powder recorded at 77 K and 300 K were measured in the transmission geometry. The spectrometer had a constant acceleration of the radiation source <sup>57</sup>Co(Rh) at a velocity of  $\pm 10$  mm/s. Calibration was made by an  $\alpha$ -Fe foil and therefore the isomer shift is estimated relative to  $\alpha$ -Fe. At 300 K, only a broad central doublet is observed (superparamagnetic state). At 77 K, a spectrum typical of SPM particles is observed, consisting of the paramagnetic doublet and two sextets (ferromagnetic state) associated with maghemite tetrahedral (A) and octahedral (B) iron sites recognized, and the quadrupole splitting is negligible and hyperfine fields are below 50 T, which is a typical value of bulk maghemite [24].

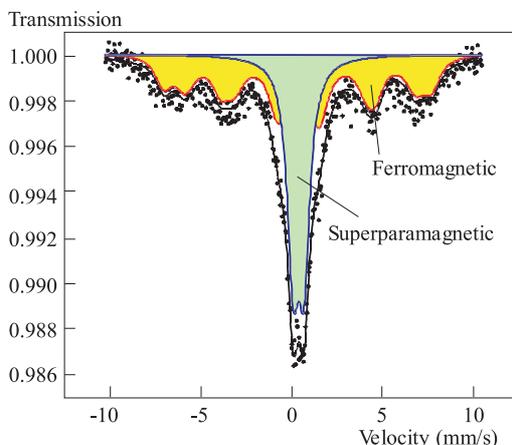
Assuming the NPs to be spherical in shape, the hyperfine field  $H_T$  obtained at the blocking temperature  $T_B$  is related through the particle size  $d$  by [24]

$$H_T = H_0 \left( 1 - \frac{3k_B T}{\pi K d^3} \right)$$

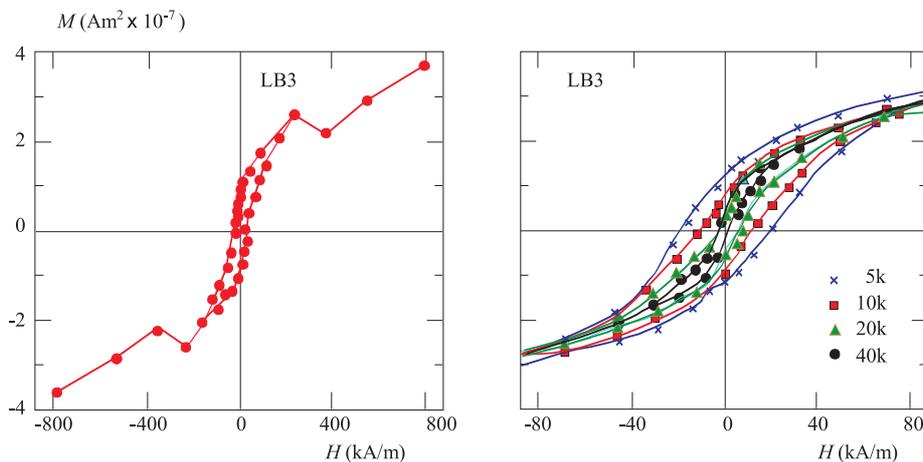
where  $H_0$  is the hyperfine field at zero temperature. Using the experimentally observed hyperfine field at 77 K ( $H_T = 45.96$  T), we obtained the mean particle size of 10 nm. Considering the areas enclosed by fitting curves in the Mössbauer spectrum approximately 40% of NPs are still in SPM (or PM) state (see Fig. 3). The Mössbauer spectrum agrees well with the predicted blocking temperature range; at the liquid nitrogen temperature only particles with a diameter exceeding 12.7 nm are in the FM state. The difference between experimentally observed SPM-FM ratio and theoretically predicted (from



**Fig. 2.** Blocking temperature as a function of magnetic nanoparticle (NP) diameter (left view). NP size distribution estimated from scanning electron microscopy (analyzed image shown in the inset). Dashed line separates ranges of ferromagnetic and superparamagnetic NPs at liquid nitrogen temperature (77 K)



**Fig. 3.** Mössbauer spectrum recorded at a temperature of 77 K. Solid line represents the best fit consisting of a doublet (superparamagnetic state) and two sextets (ferromagnetic state).



**Fig. 4.** Vibration magnetometry measurement of hysteresis at temperature range 540 K (left) and its detailed view (right)

SEM micrograph) can be explained by the presence of PM impurities, whose amount is about 10% (excess of PM obtained from comparison of the Mössbauer spectra with the ratio predicted from SEM). Detailed information about the fitted composition is shown in Table 1.

The ratio of tetrahedral and octahedral positions of iron atoms  $[Fe^{3+}]_{Octahedral}/[Fe^{3+}]_{Tetrahedral} \approx 1.48$  which corresponds with maghemite structure (1.66). The devia-

tion from the theoretical value predicts impurities of other structures.

Vibration magnetometry recordings exhibit a hysteresis at low temperatures as shown in Fig. 4. A linear increase of magnetization  $M$  at higher fields may be referred to the paramagnetic impurities, which is observed temperature-dependent below ca. 50 K. The hysteresis is most pronounced at the lowest temperatures and the

**Table 2.** Averaged measured values of coercive field ( $H_c$ ) and remanent magnetization ( $M_r$ ) as a function of temperature ( $T$ ).

T (K)	$H_c$ (kA/m)	$M_r$ (nTcm <sup>3</sup> )
5	19.38	5.50
10	10.94	4.50
20	5.01	2.50
40	1.19	1.65

coercive field  $H_c$  is about 19 kA/m, which is comparable with the bulk value of 24 kA/m. The ratio of remanent magnetization  $M_r$  is also highest at 5 K and it is about 0.37 nTcm<sup>3</sup>, which may be compared with the bulk value of 0.5 nTcm<sup>3</sup>. The values of  $H_c$  and  $M_r$  parameters of the hysteresis loops are shown in Table 2. The  $H_c$  rapidly decreases with temperature and the hysteresis ceases above 50 K.

## 5 SUMMARY

Two-dimensional systems of  $\gamma$ -ferrite (maghemite) NPs with well-defined thicknesses were prepared by the Langmuir-Blodgett technique. The analysis of the Mössbauer spectrum confirms NP composition and the hyperfine field decrease was used for estimation of the particle mean size (about 12 nm). The distribution in NP diameter leads to the wide range of the blocking temperature, which is observed in the SPM-FM phase ratio in the Mössbauer spectrum at 77 K. A difference between predicted and experimentally recorded ratio can be accounted for by PM impurities. Vibration magnetometry above 50 K indicates that a majority of the measured NP system is in the SPM state. The FM state dominates below 50 K, the hysteresis is most pronounced at the lowest temperature of the experiment, at 5 K, exhibiting the highest  $H_c$  as well as  $M_r$ . The coercive field ( $H_c$ ) as well as the hyperfine field ( $H_T$ ) are slightly decreased in comparison with the bulk parameters, the fact which is in accordance with the theory of domain size-dependent magnetic behaviour (so-called size-effect). Moreover, the wide range of SPM-FM phase transition shown in the Mössbauer spectrum and vibration magnetometry is induced by the size-dispersion of NPs as well as the composition of NPs. The assumed dispersion of NPs was confirmed by scanning electron images (Fig. 2).

As we had shown, the magnetic properties strongly depend on NP size and temperature. Therefore, exploitation of NP arrays for magnetic memories requires a precise control of various NP properties (NP size, impurities, deposition), which are mostly determined by preparation conditions.

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