

STRUCTURE, COMPOSITION AND MAGNETIC PROPERTIES  
OF FERROFLUID NANOPARTICLES AFTER SEPARATIONG. Kronkalns<sup>1</sup>, M. Kodols<sup>2</sup>, M.M. Maiorov<sup>1</sup><sup>1</sup>Institute of Physics, University of Latvia,  
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The structure, composition and magnetic properties of iron oxide nanoparticles are studied as dependent on the synthesis technology and method of separation in ferrofluids. The goal of the present study is to improve the magnetic properties of wet-synthesized nanoparticles and achieve a narrow nanoparticle size distribution. The results of measurements show that by varying the conditions of the chemical coprecipitation method, different compositions and structures of the nanoparticles could be obtained. The separation of ferrite nanoparticles of a polydisperse colloid by centrifugation as well as by HGMS provides the possibility to obtain a nanoparticle set with narrow size distribution.

**Key words:** *ferrofluids, iron oxide nanoparticle structure, magnetic properties.*

## 1. INTRODUCTION

Ferrofluids (FFs) are dispersions of single magnetic domain nano-sized particles suspended in a carrier liquid. Colloidal stability is achieved by coating the particles with surfactant molecules. The most commonly used material of nanoparticles in FFs is the inverse spinel (magnetite). The spinel structure is formed by a nearly close-packed face-centred cubic array of anions with holes partly filled with cations. In the general case, the distribution of cations in spinel ferrites can be described by the formula:  $\text{Me}_\delta^{2+}\text{Fe}_{1-\delta}^{3+}[\text{Me}_{1-\delta}^{2+}\text{Fe}_{1+\delta}^{3+}]\text{O}_4$ , where the ions occupying tetrahedral (A) sites are written before the brackets, the ions replaced in octahedral (B) sites are in the brackets, and  $\text{Me}^{2+} = \text{Mn}, \text{Zn}, \text{Mg}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Cd}$ . Parameter  $\delta$  describes the degree of inversion. For the random cation distribution  $\delta = 1/3$ , and for the normal spinel structure  $\delta = 0$ . In the inverse spinel structure one half of the trivalent cations occupy the tetrahedral sites, while the other half and all of the divalent cations – the octahedral sites [1].

Magnetite ( $\text{Fe}_3\text{O}_4$ ) is an inverse spinel with one half of  $\text{Fe}^{3+}$  ions in A sites and the rest (i.e.  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  ions) in B sites. The bulk magnetite is usually produced at  $T > 1000$  K by direct solid-state reactions between simple iron oxides. The production of magnetite nanoparticles for FF requires a special technology.

Ultrafine magnetite particles are produced by a chemical co-precipitation method at the temperatures below 373 K.

The formation of a single nanoparticle depends on random local physical-chemical conditions [2] (temperature, pressure, concentration, pH, mixing rate) as well as on the type and purity of reacting chemical products. The method of preparation remarkably affects the cation distribution and the formation of structural defects. For example, ferrites synthesized by the wet chemical method exhibit a wide size distribution of nanoparticles with lower values of magnetization than those prepared by standard ceramic methods. The goal of the present study is to improve the magnetic properties of wet-synthesized nanoparticles, and obtain a narrow nanoparticle size distribution. The latter is particularly important for applications in microbiology, medicine, and other branches.

## 2. EXPERIMENTAL

The structure, composition and magnetic properties of nanoparticles are investigated as dependent on the coprecipitation reaction temperature. Magnetic nanoparticles were produced at three temperatures by coprecipitation of ferric-ferrous salts (the mole ratio 2:1) with ammonium hydroxide. The particles were coated with an adsorbed layer of surfactant (oleic acid) and suspended in non-aqueous liquid (initial samples S1, S2, S3) [3].

The centrifugation at acceleration 7000 g applied to the thin FF layer and the method of high-gradient magnetic separation (HGMS) [4] were used for the fractionation of initial synthesized colloids. The HGMS is based on a thin ferromagnetic 40  $\mu\text{m}$  wire matrix in external magnetic field of intensity 5 kOe. The magnetic phase powder specimens were produced by the method of vacuum evaporation of carrier fluid at 323 K. A thin layer of freshly prepared FF sample S3 is centrifuged at 7000 g for 8 h. After centrifugation, two samples are taken from the upper (S4) and lower (S5) portions of the centrifuged FF. The second portion of sample S3 is passed through a HGM separator to obtain samples S6 (light fraction) and S7 (dark fraction). The magnetic powder specimens are made from these samples for X-ray investigation by evaporation of the carrier fluid at 323 K.

The structure and size of the magnetic nanoparticles were investigated using a Bruker AXS diffractometer Advance 8 with a SolX detector. For quantitative analysis and crystallite size determination the Topas 4.1 software with Rietveld refinement was applied. The following crystallographic parameters, atomic coordinates for each phase and measuring parameters were taken:  $\text{CuK}_\alpha$  radiation (1.5418 Å), range 10–70  $2^\circ\Theta$  (increment 0.02  $2^\circ\Theta$ ), the time per step to reduce background effects 1 s.

The magnetic measurements were performed employing a vibration sample magnetometer (*Lake Shore Cryotronics, Inc.*, model 7404 VSM). For processing the magnetization curve the software developed at the Institute of Physics (University of Latvia) was used [5, 6]. The particle and crystallite sizes of the samples were determined by different methods: magnetization curve analysis (magnetogranulometry), dynamic light scattering (DLS) (*Zetasizer nano S90 Malvern Instruments* software, electron microscopy (JEOL Transmission Electron Microscope with 100 kV electron acceleration) and X-ray diffraction line broadening (Scherer's equation).

### 3. RESULTS AND DISCUSSION

Figure 1 displays the X-ray diffractogram of the magnetic particle powder extracted from the magnetic fluid and synthesized at  $T_c = 290$  K (sample S1) coprecipitation temperature. As seen, a perfect magnetite structure is formed with face-centred crystalline structure. Higher coprecipitation temperatures (333 K for sample S2 and 353 K for sample S3) lead to the formation of disordered structure and composition of the crystal (see Table 1). At these temperatures some ferrous ions oxidize to ferric ones, since the reaction is performed in open vessels.

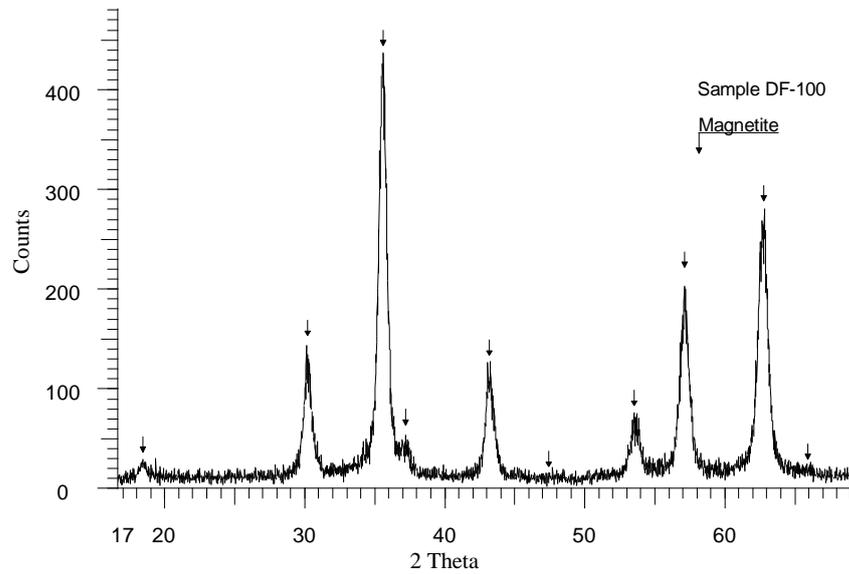


Fig. 1. X-ray diffractogram of magnetic nanoparticle powder specimen extracted from FF sample DF-100.

Figure 2 shows the particle size distribution obtained by magnetogranulometric analysis of three FF samples synthesized at different temperatures. Since the chemical reaction is exothermic, higher temperatures result in smaller nanoparticles.

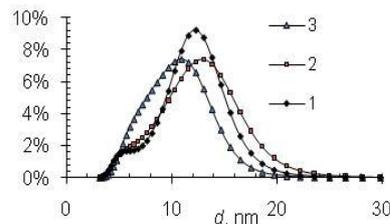


Fig. 2. The particle size distribution of FF samples obtained by magnetogranulometry and software analysis.

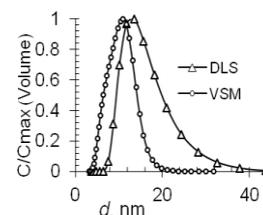


Fig. 3. The particle size distribution of FF sample S3 obtained by magnetogranulometry (VSM) and dynamic light scattering.

Figure 3 shows the size distribution of initial FF sample obtained by magnetogranulometry and dynamic light scattering. The latter method gives higher

values for nanoparticle sizes – the solid magnetic phase with a surfactant layer. In addition, as shown by X-ray diffraction pattern analysis, the nanoparticles contain some of the non-magnetic phase (goethite).

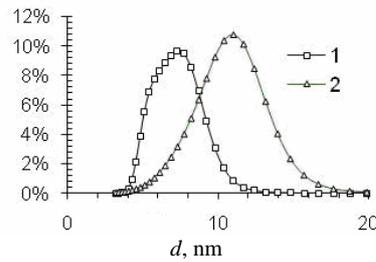


Fig. 4. The particle size distribution of sample S3 from magnetogrulometry after centrifugation: 1 – light fraction; 2 – dark fraction.

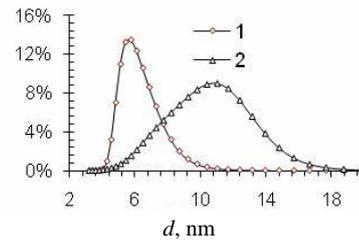


Fig. 5. The particle size distribution of sample S3 obtained by magnetogrulometry after HGMS: 1 – light fraction; 2 – dark fraction.

In Fig. 4 it is seen that centrifugation of FF samples leads to changes in the size distribution of nanoparticles and in the magnetic properties of the samples, whereas the composition of magnetic nanoparticles remains unchanged.

Figure 5 illustrates the distribution of nanoparticles of sample S3 after HGMS treatment. It is evident that HGMS alters more effectively the composition and structure of nanoparticles than centrifugation – especially the particle size distribution and the phase composition.

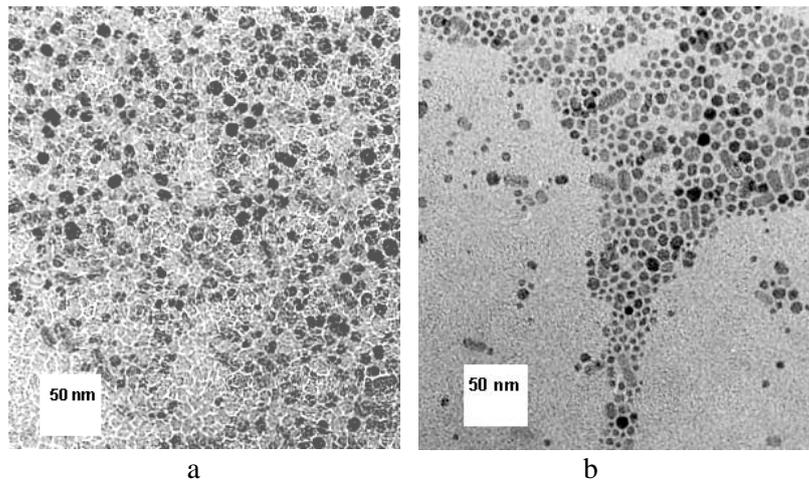


Fig. 6. Electronic micrographs of nanoparticles of centrifuged FF sample S3: a – dark fraction, b – light fraction.

Figure 6 displays the electron micrographs of the nanoparticles of centrifuged FF sample. The electron microscope images also show a change in the nanoparticle size distribution after centrifugation. The summary results of all experimental measurements are given in Table 1.

The summary properties of magnetic nanoparticle samples

Sample	Magn. size distrib. Mode, nm	Magn. size distrib. FWHM, nm	Hydro-dynam. size distrib. Mode, nm	Hydro-dynam. size distrib. FWHM, nm	Crystallite size from X-ray diffractogr., nm	Magnetic phase composition from X-ray diffractograms
S1	12.2	6.0	–	–	16.4	Magnetite – 100%
S2	13.0	8.2	–	–	12.6 12.1	Maghemite – 69.3% Magnetite – 30.7%
S3	10.6	7.7	13.7	10.6	9.5 7.9 9.3	Maghemite – 56.8% Magnetite – 17.6% Goethite – 25.6%
S4	10.8	5.2	17.2	10.1	4–12.5	Maghemite – 46.7% Goethite – 36% Magnetite – 17.6%
S5	7.3	4.3	10.6	6.2	12.6 11.8 4.3	Maghemite – 55.6% Goethite – 26.8% Magnetite – 17.6%
S6	10.5	6.3	15.1	9.4	10.1 7.4	Goethite – 69.4% Maghemite – 30.6%
S7	6.1	2.4	16.8	11.4	11 9.2 5.1	Maghemite – 54.5% Magnetite – 36.6% Goethite – 8.9%

#### 4. CONCLUSIONS

By varying the conditions of the chemical coprecipitation method, different compositions and structures of the nanoparticles can be produced. The separation of ferrite nanoparticles of a polydisperse colloid by centrifugation as well as by HGMS provides the possibility to obtain a nanoparticle set with narrow size distribution. In the work it is shown that choosing appropriate methods of synthesizing the nanoparticles and of ferrofluid separation allows making the magnetic material with required properties.

#### ACKNOWLEDGEMENTS

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## FEROMAGNĒTISKO ŠĶIDRUMU NANODAĻIŅU STRUKTŪRAS, SASTĀVA UN MAGNĒTISKO ĪPAŠĪBU IZMAIŅAS PĒC SEPARĀCIJAS

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### K o p s a v i l k u m s

Darbā izpētītas dzelzs oksīda nanodaļiņu struktūras, sastāva un magnētisko īpašību izmaiņas atkarībā no sintēzes tehnoloģijas, kā arī no dažādām feromagnētisko šķidrumu separācijas metodēm. Magnētisko nanodaļiņu struktūra, sastāvs un izmērs tika pētīts ar rentgenstaru difraktometru un transmisijas elektronu mikroskopu. Daļiņu magnētiskās īpašības tika mērītas ar vibrācijas magnetometru. Pētījumā parādīts, ka, mainot magnētisko nanodaļiņu sintēzes apstākļus, kā arī, separējot feromagnētisko šķidrumu ar dažādām metodēm, var izgatavot paraugus ar nepieciešamajām specifiskajām īpašībām.

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