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BOOK OF ABSTRACTS

VOLUME II

THE MANIFESTATION OF STOICHIOMETRY DEVIATION IN SILICA-COATED MAGNETITE NANOPARTICLES

S.V. Stolyar[1,2], *D.A. Velikanov*[2*], *A.V. Tyumentseva*[1], *S.V. Komogortsev*[2], *R.N. Yaroslavtsev*[1,2], *Yu.V. Gerasimova*[2], *M.V. Rautskii*[2], *R.S. Iskhakov*[2]

[1]Krasnoyarsk Scientific Center, Federal Research Center KSC SB RAS, Krasnoyarsk, Russia
[2]Kirensky Institute of Physics, Federal Research Center KSC SB RAS, Krasnoyarsk, Russia
[*]E-mail: dpona1@gmail.com

In recent years, magnetic nanoparticles based on iron oxides have attracted interest in practical applications in the field of biotechnology and biomedicine [1]. Surface-modified magnetic nanoparticles can be used for selective isolation of certain biomolecules, such as nucleic acids and proteins. The method, commonly known as "magnetic separation", has gained popularity in performing tests for diagnostic purposes [2].

The synthesis of magnetic nanoparticles was carried out by the method of chemical coprecipitation of iron salts $FeCl_3$ and $FeCl_2$ in a molar ratio of 2:1 in an aqueous solution. Tetraethoxysilane (TEOS) was used to coat magnetic nanoparticles with silicon oxide. Magnetic nanoparticles were coated in ethanol:water mixture in a 9:1 ratio with the addition of TEOS in two versions: 50 mg nanoparticles per 250 µl TEOS (sample A Fe_3O_4:SiO_2 = 1:1.3) and 50 mg nanoparticles per 800 µl TEOS (sample B Fe_3O_4: SiO_2 = 1:4.5).

The magnetization curves measured in the range from –15 to 15 kOe are symmetric about the origin and contain a reversible part as well as an irreversible part – a hysteresis loop (Fig. 1). The coercive force, remanent magnetization, and magnetization in a field of 15 kOe decrease with increasing temperature. Low values of the coercive field indicate that particles with this size are close to the transition to the superparamagnetic state.

The relatively small values of the saturation magnetization of nanoparticles are due to the silica shell. This can be used for an independent assessment of the ratio of magnetite and silica, originally

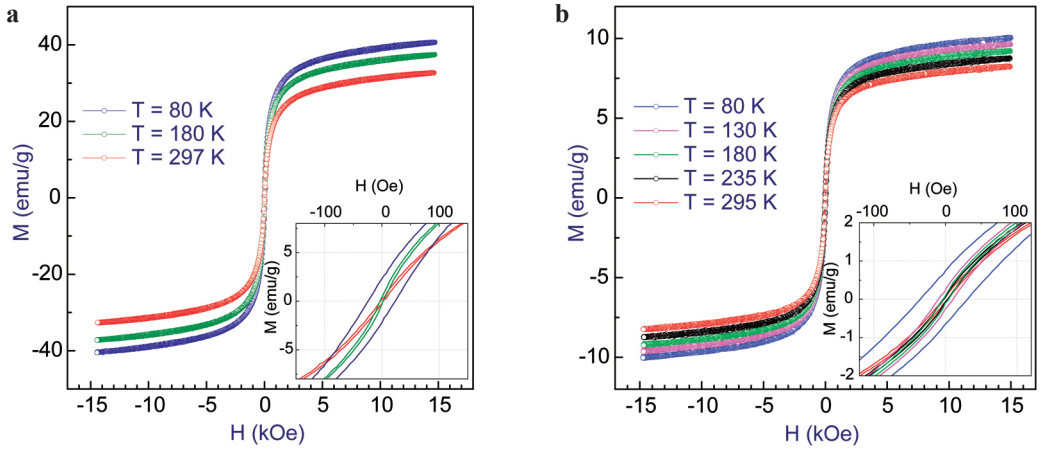

Figure 1. Hysteresis loops of magnetic nanoparticles. **a** Fe_3O_4:SiO_2 = 1:1.3, **b** Fe_3O_4:SiO_2 = 1:4.5.

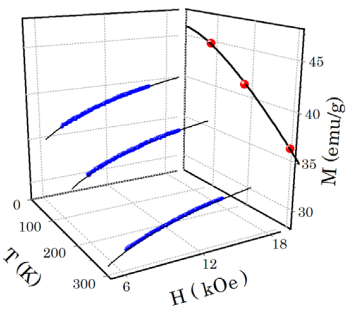

Figure 2. Determination of M_{s0} from the magnetization curves of particles in the region of approaching magnetization to saturation. Blue symbols – measured $M(H)$, thin black lines – fitting by Eq. (1), red symbols – saturation magnetization estimated from Eq. (1), black thick line – description of $M_s(T)$ by Eq. (2).

made on the basis of the technological filling of the components during the synthesis. For such an estimate, we determined the magnetizations of the two studied samples of the composite material in a state of complete magnetic saturation and zero temperature (M_{s0}). As can be seen from Fig. 2, the magnetization does not reach saturation even in the maximum fields used (15 kOe) and decreases with increasing temperature; therefore, we determined M_{s0} as follows. It was found that at a stabilized temperature in high fields, the magnetization of nanoparticles approaches saturation according to the equation [3]:

$$M(H) = M_s\left(1 - \frac{1}{15}\frac{H_a^2}{H^{1/2}(H^{3/2} + H_R^{3/2})}\right), \quad (1)$$

where M_s – saturation magnetization, H_a – anisotropy field, H_R – exchange field in the core-shell system. Indeed, in our case, Eq. (1) makes it possible to describe the magnetization curves in high fields and estimate the quantitative values of M_s for different temperatures.

The change in the M_s value in magnetite nanoparticles with temperature is described by Bloch's law $T^{3/2}$:

$$M_s(T) = M_{s0}(1 - B \cdot T^{3/2}) . \quad (2)$$

Extrapolation of the data to 0 K according to Eq. (2) (Fig. 1) gives an estimate of M_{s0} (Table 1). Since the magnetization of silica is zero, the magnetization of the composite particle is related to the weight fraction of magnetite nanoparticles X_m and their magnetization M_{s0_m} as $M_{s0} = X_m \cdot M_{s0\_m}$. Using the measured value M_{s0} and the weight fraction of magnetite Xm, we estimated the magnetization of nanoparticles reduced only to the weight of magnetite M_{s0_m} (see Table 1). As is known, the magnetization of pure quasi-spherical magnetite nanoparticles M_{s0_m} is lower than the

Table 1. Saturation magnetization of particles at 0 K.

Sample	$X_{Fe_3O_4}$ at synthesis	M_{s0}, emu/g	Estimate of M_{s0} of pure magnetite particles
A	1/(1+1.3) ≈ 0.435	46.0 ± 0.2	105
B	1/(1+4.5) ≈ 0.182	10.9 ± 0.2	60

magnetization of bulk magnetite crystals (92 emu/g) and depends on their size. For particles with an average size of 10 nm (our case), according to [4], the magnetization should be $M_{s0\_m} \approx 26$ emu/g. It can be seen from Table 1 that the magnetization of nanoparticles is significantly higher and that the magnetization of magnetite in the composition of the two studied samples is different. This can be interpreted as stoichiometric displacement in the composition of Fe_3O_4@SiO_2 nanoparticles from standard Fe_3O_4. In addition, we also find an indication that this stoichiometric displacement is different in samples with different weights of magnetite and silica (the difference in magnetization in Table 1). Different stoichiometry in magnetite means that the stoichiometry of the silicate coating will also differ, i.e. it will have varying potencies in the isolation of nucleic acids.

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