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Magnetite Nanocrystals with a High Magnetic Anisotropy Constant due to the Particle Shape

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Abstract—Chemical solution deposition in the presence of arabinogalactan makes it possible to prepare magnetite nanocrystals in the form of square plates with a high aspect ratio (~1/9). The magnetic anisotropy constant of particles is several times higher than that of spherical magnetite particles, which enhances the hysteretic properties with a small particle volume retained.

Keywords: magnetite, nanoparticles, magnetic anisotropy, polysaccharide.
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The use of ferromagnetic nanoparticles in biomedicine (e.g., for magnetic separation, drug delivery, microsurgery, magnetic hyperthermia, and as contrast agents in magnetic resonance tomography) makes it urgent to optimize their magnetic properties [1–4]. Superparamagnetic particles (up to 20 nm in size) are smaller than ferromagnetic particles (particles in the blocked state) and characterized by a magnetic moment that is several orders of magnitude smaller and zero magnetic hysteresis. This specific feature of superparamagnetic particles facilitates the formation of stable colloidal solutions but deteriorates significantly the mechanical and thermal effects. In this context, the preparation of ferromagnetic particles as small as possible is of interest. The main criterion for stabilization of the magnetic-moment direction can be set by the inequality [5]

$$k_B T < KV / \ln(\tau/\tau_0), \quad (1)$$

where K is the magnetic anisotropy constant of a particle, V is its volume, T is the temperature of the medium, τ is the characteristic time of using the particle as a permanent magnet or particle measurement time, k_B is the Boltzmann constant, and τ_0 is the characteristic time of transition between two directions of the particle magnetic moment under thermal fluctuations (~10^{-9} s).

According to (1), at small particle volumes, the stabilization can be implemented only by increasing constant K. The effective magnetic anisotropy constant can be increased by increasing the contributions from the magnetocrystalline anisotropy [6], magnetic shape anisotropy [7], and surface magnetic anisotropy [8]. For magnetite (Fe_3O_4) nanoparticles, which are attractive in view of their biocompatibility, the first contribution related to the chemical composition and structure of the particle can hardly be increased. Variations in the particle form and surface make it possible to increase the two remaining contributions. In this Letter, we demonstrate that the magnetic anisotropy constant of magnetite nanocrystals shaped as square plates with a high aspect ratio (~1/9) is several times larger than the constant of spherical magnetite particles, which enhances the hysteretic characteristics with the small particle volume retained.

The use of natural polysaccharides as stabilizing and restoring agents is a promising line of research in the synthesis of nanoparticles of different types for biomedicine with a wide spectrum of bactericidal, conducting, and magnetic properties [9, 10]. Nanoparticles can be prepared using polysaccharide both by a single chemical reaction [9] and in two steps (magnetic particles are first synthesized,

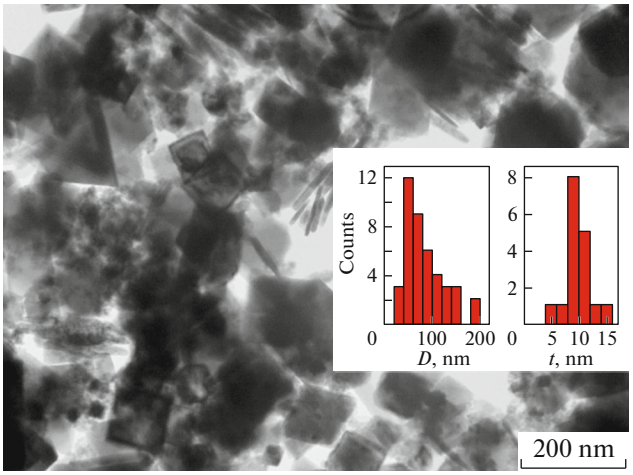

Fig. 1. TEM images of particles and (inset) their distributions over square size D and plate thickness t.

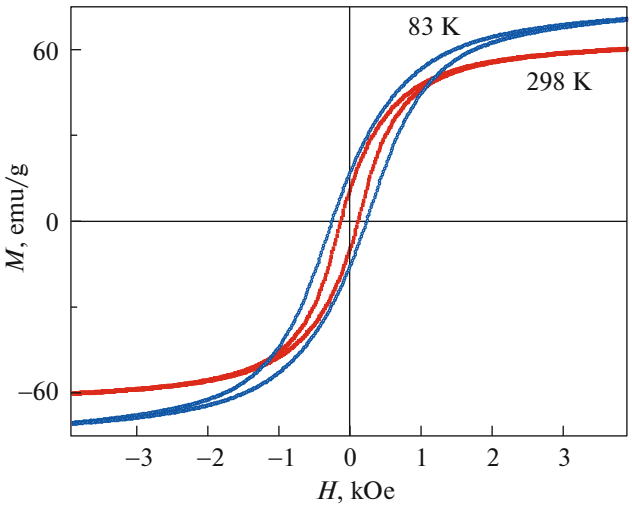

Fig. 2. Hysteresis loops in magnetite nanocrystals.

and then their surface is modified by polysaccharide [10]). Another known method for preparing these composite nanoparticles is the use of microorganisms [11, 12]. Arabinogalactan is a new polysaccharide, which is successfully used for synthesizing nanoparticles [13].

In this study, magnetite nanoparticles were obtained by chemical solution deposition from iron sulfate ($FeSO_4 \cdot 7H_2O$) in the presence of arabinogalactan served as a structure-directing and stabilizing agent. The required temperature (80°C) was maintained using an aqueous thermostat. Electron microscopy analysis was carried out on a Hitachi HT7700 transmission electron microscope (TEM) (accelerating voltage 100 kV) at the Center for Collective Use of the Krasnoyarsk Science Center (Siberian Branch, Russian Academy of Sciences). The Mössbauer spectra were recorded on an MS-1104Em spectrometer with a $^{57}Co(Cr)$ source at room temperature. Static magnetic measurements were carried out with a vibrational magnetometer at field strengths up to 6 kOe and in the temperature range of 77–300 K. The insert with an empty capsule for powder was measured separately and its contribution (~1%) was subtracted from the total signal.

The electron microscopy images (Fig. 1) show that nanoparticles are shaped as square plates with mean sizes of 90 × 90 × 10 nm (the thickness and width distributions of the particles are shown in the insets in Fig. 1). In the high-resolution images of the surfaces of individual plates, one can see systems of crystalline planes uniformly filling this surface. According to the electron diffraction patterns and Mössbauer spectra, the particles under study are magnetite with a spinel structure containing a small amount of cation vacancies $(Fe^{3+})[Fe^{2+}_{0.658}Fe^{3+}_{1.228}\square_{0.114}]O_4$, where $\square$ indicates a cation vacancy.

Coercive force $H_c(T)$ decreases with an increase in temperature (Fig. 2): $H_c(83\ \text{K}) = 250 \pm 10$ Oe and $H_c(298\ \text{K}) = 125 \pm 10$ Oe. Taking into account that the coercive field should decrease according to the law $H_c = H_c(0)(1 - (T/T_B)^{0.77})$ (T_B is the blocking temperature), which is characteristic of nanoparticles [14, 15], one can estimate the coercive field at 0 K as $H_c(0) = 320 \pm 20$ Oe.

The approaching of magnetization to saturation is adequately described by the following expression (see Fig. 3):

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

which was proposed for describing magnetization curves of iron oxide nanoparticles in [16] and successfully applied in [17].

Parameters M_s and H_a characterize, respectively, the magnetization and local magnetic anisotropy field of nanoparticles and are assumed (for the best fitting at room temperature) to be equal to $M_s = 62 \pm 1$ emu/g (per a volume of 330 G) and $H_a = 3520 \pm 20$ Oe. Parameter H_R has the meaning of an exchange field, which characterizes the interaction between the magnetically disordered surface and ordered particle nucleus [16] (for the best fitting of the curve measured at room temperature, $H_R = 2000 \pm 20$ Oe). The term χH in formula (2) takes into account the contributions to the magnetization from both the paramagnetic susceptibility in high fields and the spin-glass shell, which is characteristic of iron oxides nanoparticles [18].

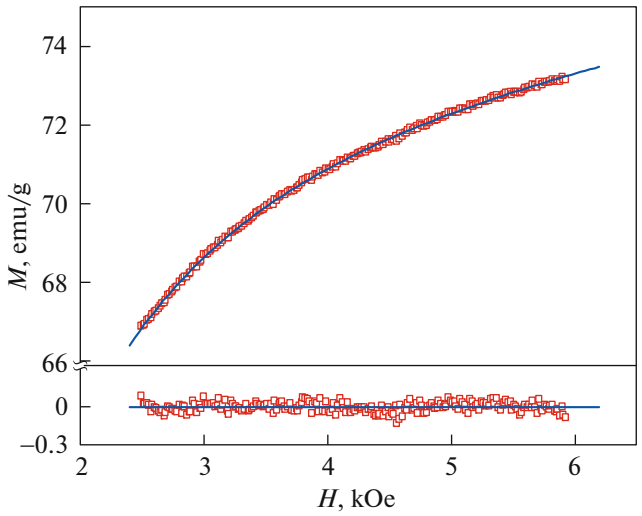

Fig. 3. Approaching of magnetization to saturation of magnetite nanoparticles at $T = 83$ K. The solid line is the best fitting using Eq. (2). The difference between the theoretical and measured values is shown at the bottom.

The anisotropy constant can be recalculated from the local magnetic anisotropy field as $K = H_a M_s/2$. For the particles under study, this parameter was $K = (5.81 \pm 0.16) \times 10^5$ erg/cm^3. The anisotropy constant of nanocrystals shaped as square plates can be estimated as a sum of the contributions from the magnetic shape anisotropy $K_{sh} = \pi M_s^2$, magnetocrystalline anisotropy $K_u = 1.3 \times 10^5$ erg/cm^3, and surface magnetic anisotropy ($k_s = 2.9 \times 10^{-2}$ erg/cm^2 [19]). The sum of these three contributions for nanoparticles $90 \times 90 \times 10$ nm in size is $K = 6.3 \times 10^5$ erg/cm^3, which is in good agreement with the measured anisotropy constant. The measured anisotropy constant of the plates is several times larger than the constant of spherical particles because of the significant contribution from the magnetic shape anisotropy and larger surface contribution. This should lead to the thermal stabilization (blocking) of the magnetic moment for magnetite particles with much smaller volume. A stronger magnetic hysteresis may be expected for these particles. Indeed, the experimental coercive force $H_c(0\ \text{K})$ was found to be 0.32 kOe, whereas the coercive force in spherical magnetite particles generally does not exceed 0.1 kOe [20].

To conclude, the following should be mentioned. It was shown that chemical solution deposition in the presence of arabinogalactan makes it possible to prepare magnetite nanocrystals in the form of square plates with a high aspect ratio (~1/9). The magnetic anisotropy constant of these particles is several times larger than that of spherical magnetite particles, which enhances the hysteretic properties with the small particle volume retained.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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