Collective Spin Glass State in Nanoscale Particles of Ferrihydrite

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Abstract—Ferromagnetic resonance was used to study three types of ferrihydrite nanoparticles: nanoparticles formed as a result of the cultivation of microorganisms *Klebsiella oxytoca*; chemically prepared ferrihydrite nanoparticles; chemically prepared ferrihydrite nanoparticles doped with Cu. It is established from the ferromagnetic resonance data that the frequency-field dependence (in the temperature range $T_P < T < T^*$) is described by the expression: $2\pi\nu/\gamma = H_R + H^A_{(T=0)}(1 - T/T^*)$, where γ is the gyromagnetic ratio, H_R is the resonance field. The induced anisotropy H^A is due to the spin-glass state of the near-surface regions. T_P temperature characterizes the energy of the interparticle interaction of nanoparticles.

Keywords: nanoparticles, ferrihydrite, magnetic anisotropy, magnetic resonance

INTRODUCTION

The size of the ferrihydrite nanoparticles, which is a magnetic semiconductor, is in a narrow range of up to 8 nm. The transformation $Fe_2O_3 \cdot nH_2O \rightarrow Fe_2O_3$ occurs as the particle sizes increase. Ferrihydrite plays a huge role in the metabolism of living organisms because it is formed in the core of the protein complex of ferritin. The majority of magnetic studies was performed on ferritins (horse spleen ferritin) and ferrihydrites obtained chemically. According to the results of these studies, ferrihydrite is an antiferromagnet with a Néel temperature $T_N = 340$ K [1]. The superparamagnetic blocking temperature can vary up to ∼100 K as a function of the origin of the nanoparticles and their size. At low temperatures, the magnetization curves are characterized by magnetic hysteresis and exchange bias (after cooling in an external field) [2–4]. The temperature dependences of the coercive field and the exchange bias field are usually correlated. The resonance properties of ferrihydrite nanoparticles were studied in [5–7]. Interactions between nanoparticles have a significant effect on superparamagnetic relaxation. Although the dipole interaction between neighboring antiferromagnetic nanoparticles is small, the exchange interaction between the surface atoms of neighboring nanoparticles plays a large role at low temperatures. Collective effects due to the interaction of nanoparticles can lead to spin-glass-like states [8].

The purpose of this work is to study ferrihydrite nanoparticles by the method of ferromagnetic resonance. We investigated three types of nanoparticles: nanoparticles formed as a result of the cultivation of microorganisms *Klebsiella oxytoca*; chemically prepared ferrihydrite nanoparticles; chemically prepared ferrihydrite nanoparticles doped with Cu.

1. EXPERIMENTAL

Nanoparticles of biogenic ferrihydrite are synthesized as a result of the cultivation of microorganisms. The bacterium *Klebsiella oxytoca* under anaerobic conditions can synthesize secretory exopolysaccharide [9–12], which is associated with nanoparticles of ferrihydrite. The synthesized biogenic powders are ferrihydrite nanoparticles coated with polysaccharides. This shell significantly weakens the interactions between ferrihydrite nanoparticles, which makes it possible to assess the contribution of interparticle interactions to the magnetic properties of the material.

Synthetic ferrihydrite nanoparticles are synthesized as a result of the reaction of Fe^{3+} iron salt and alkali solution. The addition of Cu salt to the solution in the preparation of ferrihydrite nanoparticles by a chemical method led to the doping of the nanoparticles. Electron microscopic studies of the resulting nanoparticles were carried out on a Hitachi HT7700
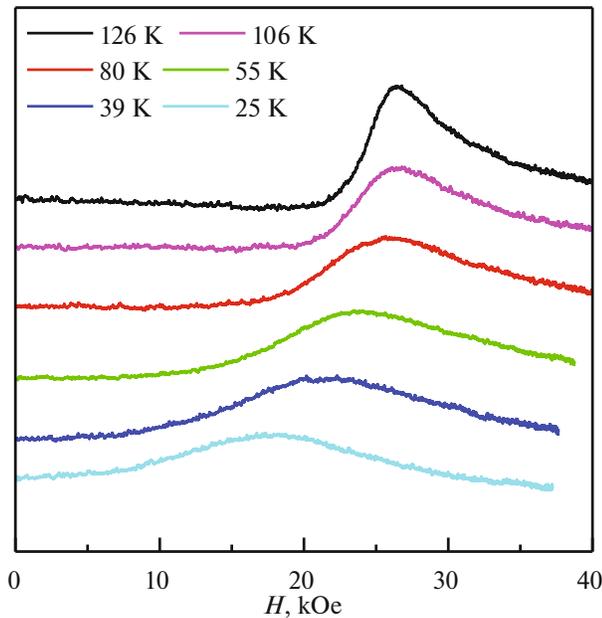
Fig. 1. Ferromagnetic resonance spectra of synthetic ferrihydrite measured at a frequency of 76 GHz.

Fig. 2. Frequency−field dependences of synthetic ferrihydrite at temperatures of 4.2 and 150 K.

transmission electron microscope (accelerating voltage of 100 kV). The sizes of the studied nanoparticles were 2−3 nm. Magnetic resonance studies were carried out using an original setup [13], which makes it possible to obtain frequency−field dependences in a wide range of fields, frequencies and temperatures.

2. RESULTS AND DISCUSSION

The ferromagnetic resonance spectra of synthetic ferrihydrite nanoparticles were measured in the temperature range from 4 to 150 K. Figure 1 shows the characteristic absorption spectra. With decreasing temperature, there is a broadening of the absorption line and a shift in the resonance field toward lower fields.

Figure 2 shows the frequency−field dependences for two temperatures: 4.2 and 150 K. The figure shows that at $T = 4.2$ K $\nu(H)$ is characterized by a gap, which depends on temperature. This gap indicates the presence of induced rotational anisotropy in the ferrihydrite nanoparticles [14]. Using the values of the resonance fields, the temperature dependences of the anisotropy field were determined, which are shown in Fig. 3 for two frequencies of 76 and 26 GHz. Figure 3 shows that the induced anisotropy field H_R linearly depends on temperature in the range $T_p < T < T^*$. At $T^* \approx 60$ K $H_R \rightarrow 0$. The behavior of the anisotropy field at $T < T_P$ indicates the presence of another type of interaction in chemically synthesized nanoparticles of ferrihydrite. This additional interaction mechanism turns off at $T = T_P$. For comparison, the inset in Fig. 3 shows the dependence of the induced anisotropy field
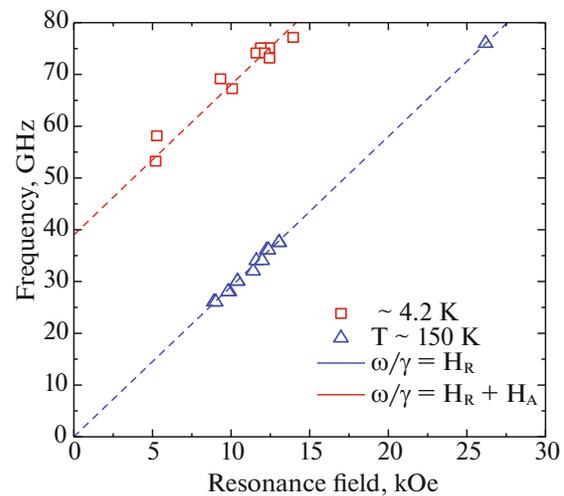
$H_A(T)$ of ferrihydrite nanoparticles coated with a polysaccharide shell [7]. For biogenic ferrihydrite nanoparticles, the T_P temperature is absent.

The presence of induced anisotropy indicates the freezing of this subsystem of spins, i.e., the transition to a spin-glass state at a temperature T^* above which the subsystem of surface spins goes into the paramagnetic state. Table 1 shows the results of a study of ferrihydrite nanoparticles by FMR method ($\nu \sim$ 75 GHz). The presence of a large specific surface in magnetic nanoparticles leads to the formation of surface anisotropy due to a violation of the coordination numbers of surface atoms [15]. High values of surface
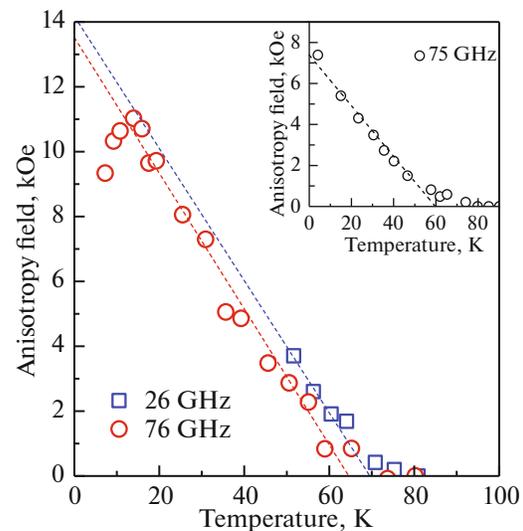

Fig. 3. Temperature dependences of induced anisotropy fields of at frequencies of $\nu = 26$ and 76 GHz. The inset shows the temperature dependence of the anisotropy field for biogenic ferrihydrite.

Table 1. Spin-glass transition temperature and anisotropy field of ferrihydrite samples

	BioFerr	SynthFerr	SynthFerr + Cu(5%)
H_A, Oe	7.66	13.52	14.9
T^*, K	55	64	56
T_P, K	–	14	16

anisotropy in ferrihydrite nanoparticles are also due to structural features consisting of surface depletion of the nanoparticle [16]. The effect of surface depletion leads to the fact that the density of the surface regions is less than the density of the central part of the particle. The configurations of cation−cation bonds in the surface region should lead to frustration of exchange interactions and the formation of a spin-glass state.

Ferrihydrite nanoparticles with a magnetic moment interact with each other, which can lead to a "collective spin glass" state at low temperatures. We believe that at $T < T_P$, collective effects play a decisive role, due to the interaction of chemically synthesized ferrihydrite nanoparticles. In the case of ferrihydrite nanoparticles coated with a polysaccharide coating, this effect is absent.

CONCLUSIONS

In this paper, ferrihydrite nanoparticles were investigated by ferromagnetic resonance. The temperature of the spin-glass transition and the anisotropy field of ferrihydrite samples are estimated. High values of surface anisotropy are due to the fact that the density of the surface regions is lower than the density of the central part of the particle. This leads to the formation of a spin-glass state in the surface regions. In the case of chemically synthesized ferrihydrite, a transition to the state of collective spin-glass was detected.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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