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Studying the Ferromagnetic Resonance Heating of an Isotropic Superparamagnet by the Example of Biogenic Ferrihydrite Nanoparticles

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Abstract—Ferrihydrite nanoparticles are synthesized and characterized. The dependences of heating of powders are studied upon pumping by a high-frequency electromagnetic field on a dc magnetic field. It is shown that the experimental dependence of the temperature of particles on a dc magnetic field is consistent with the theory of ferromagnetic resonance for an isotropic superparamagnet.

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INTRODUCTION

The temperature of ferromagnetic nanoparticles in an ac magnetic field rises upon switching the magnetization. This can be used to heat biological tissues during hyperthermia—an alternative way of treating cancer in which tissues are brought to (41–45)°C [1]. The authors of [2, 3] proposed using ferromagnetic resonance (FMR) to heat magnetic powders.

The motion of the vector of magnetization M in external magnetic field H_{eff} is described by the Landau–Lifshitz equation [4]

$$\dot{\vec{M}} = -\gamma\vec{M}\times\vec{H}_{\text{eff}} - \frac{\gamma\xi}{M}\vec{M}\times\left(\vec{M}\times\vec{H}_{\text{eff}}\right), \tag{1}$$

where γ is the gyromagnetic ratio and ξ is the damping parameter.

The temperature dependence of magnetization M_z of superparamagnetic particles is described by the Langevin function [4]

$$\langle M_z/M\rangle = L(\sigma) = \coth\sigma - \sigma^{-1}, \tag{2}$$

where $\sigma = MVH/kT$; M is the magnetization at 0 K; V is the particle volume; k is the Boltzmann constant; and T is the temperature.

If magnetization M is affected along with magnetic field H by a microwave field with frequency ω and amplitude h orthogonal to external field H, we observe the resonant absorption of microwave energy (FMR). FMR frequency ω_0 of an isotropic superparamagnet depends on parameter η of effective relaxation [4]:

$$\omega_0 = \gamma H\left(1+\eta^2\right),\ \ \eta = \xi\left(L^{-1} - \sigma^{-1}\right). \tag{3}$$

With circular polarization, the power of the high-frequency field absorbed by the unit volume of an isotropic superparamagnet is described by the equation [4]

$$P = \frac{L\eta\omega^2\gamma h^2 M}{(\gamma H - \omega)^2 + (\eta\gamma H)^2}. \tag{4}$$

The absorbed power for a linearly polarized electromagnetic wave is [4]

$$P' = 1/2((\omega) + (-\omega)), \tag{5}$$

where P is determined by Eq. (4).

According to our neutron diffraction data, ferrihydrite is an antiferromagnet with a Néel temperature of 350 K [5]. The saturation magnetization at 4.2 K is ~20 G [6]. Measurements of the $M(T)$ dependences in the zero-field cooling (ZFC) and field cooling (FC) modes in [7] yielded a blocking temperature of 25 K. According to the Néel–Brown relation, which describes the dependence of the blocking temperature on the period of measuring, the blocking temperature in the resonant (X-band) investigations should be around 100 K. Frequency–field dependences $\nu(H)$ for ferrihydrite nanoparticles were examined at different temperatures in [7]. The dependences were linear and

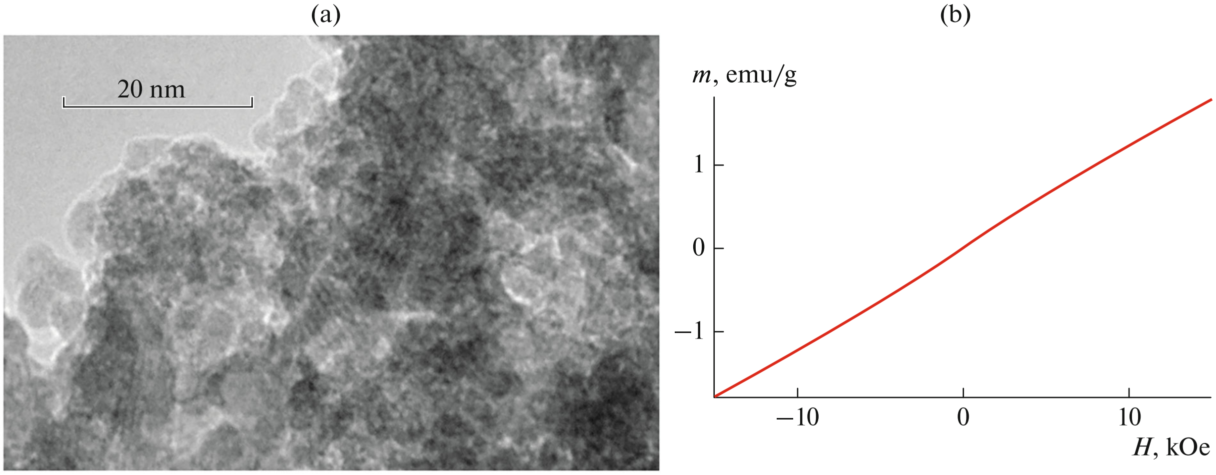

Fig. 1. (a) Microphotograph of ferrihydrite particles and (b) $M(H)$ dependence recorded at room temperature.

described by the equation $2\pi\nu/\gamma = H + H_A(1 - T/T^*)$, where H_A is the anisotropy field. At $T = 4.2$ K and $H = 0$ $2\pi\nu/\gamma = H_A$ (an anisotropic superparamagnet), we had $H_A = 7$ kOe. At high temperatures $T > T^* = 50$ K and a microwave field frequency of $f = 52$ GHz, we had $H_A = 0$. The room-temperature field–frequency dependence of ferrihydrite powders is thus described by the equation $2\pi\nu/\gamma = H$, so ferrihydrite is an isotropic superparamagnet.

In this work, we use the example of a ferrihydrite powder system to explore the dependence of the temperature of nanoparticle heating in the FMR mode at a frequency of 8.9 GHz. Experimental results are compared to theoretical dependences of the absorbed power of a microwave field for an isotropic superparamagnet [4].

EXPERIMENTAL

Ferrihydrite nanoparticles were synthesized biogenically using *Klebsiella oxytoca* bacteria [7]. The phase composition and features of the size distribution of nanoparticles were studied in [6–9]. Microphotographs of particles were taken on a Hitachi HT7700 transmission electron microscope. The static magnetic properties of particles were measured using the LakeShore VSM 8604 vibration magnetometer at the Krasnoyarsk Scientific Center's regional shared resource center. FMR curves were obtained at different temperatures on a Bruker ESR spectrometer ($f = 9.4$ GHz) at the same resource center. Particle heating under pumping by a microwave field at room temperature was measured with a Radiopan SE/X-2544 ESR spectrometer ($f = 8.9$ GHz). The temperature of nanoparticles was measured using a T-type thermocouple with copper and constantan electrodes. The signal was recorded by an H307/1 2D plotter. The investigated powder was poured into a glass test tube with an inner diameter of 2.5 mm. The powder weighed ~10 mg. The working junction of the thermocouple was placed directly into the powder. No change in temperature was detected when there was no sample during microwave pumping and magnetic field scanning in the range of 0 to 5 kOe.

RESULTS AND DISCUSSION

The average size of synthesized particles was 2–6 nm [8] (Fig. 1a). Figure 1b shows the room-temperature magnetic field dependence of magnetization that is characteristic of superparamagnetic ferrihydrite powders [6]. The magnetization at 15 kOe was 1.78 emu g^{-1}.

Figure 2a shows the temperature dependences of resonant field H_{res} and FMR linewidth ΔH ($f = 9.4$ GHz) for the dried sol produced by cultivating the biomass for 5 days [9]. Measurements were made in the 140 to 400 K range of temperatures. The $\Delta H(T)$ dependence passed through a minimum at a temperature of 350 K, due possibly to the Néel temperature.

Figure 2b presents results from investigating the temporal dependence of the particle temperature increment ΔT in different dc magnetic fields H inside a microwave field with frequency $f = 8.9$ GHz. The strongest rise in nanoparticle temperature (4.5 K) is observed for the field close to resonance ($H = 3.3$ kOe), testifying to the resonance nature of microwave energy absorption. Particles in a zero dc magnetic field are apparently heated by the effect of the electric component of the microwave radiation.

Assuming that the absorbed power is spent on heating the particles, we can write $PVdt = cm\Delta T$, where P is the power absorbed according to unit volume and Eq. (5); $c = 9.2 \times 10^6$ erg g^{-1} K^{-1} is the specific heat capacity of ferrihydrite, and $m/V = \rho = 3.8$ g cm^{-3} is its density [10]. The temperature of the particles stop chang-

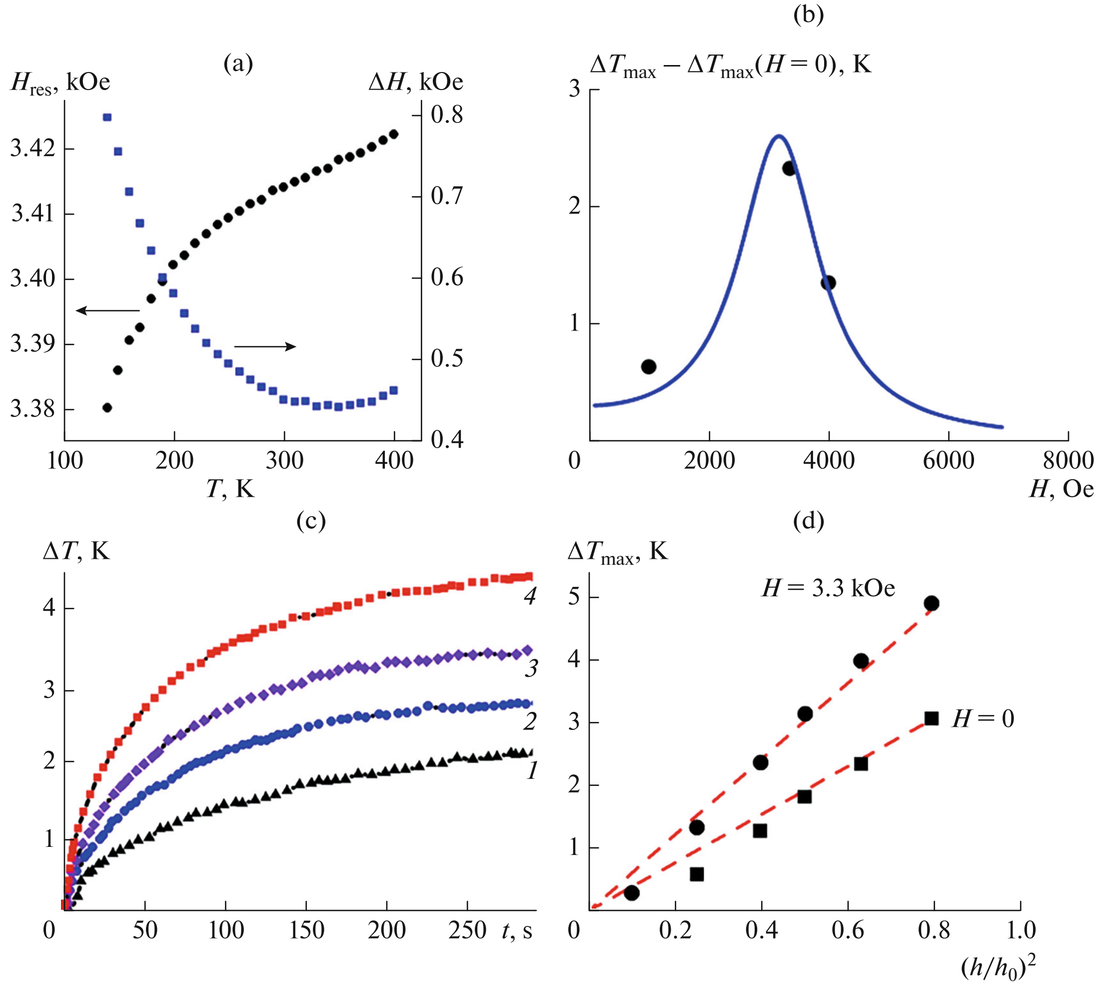

Fig. 2. (a) Temperature dependences of resonant field H_{res} and linewidth ΔH; (b) change in the temperature of ferrihydrite powders upon microwave pumping in dc fields of (*1*) $H = 0$, (*2*) 1, (*3*) 4, and (*4*) 3.3 kOe; (c) dependence of the maximum temperature increment on the squared microwave amplitude; (d) and approximation of the dc field dependence of the maximum heating and experimental points.

ing at time $t \approx 250$ s, indicating that the power absorbed by the powder has become equal to that dissipated into the environment. Assuming that heating is due only to the effect of the magnetic component of the microwave radiation, we have

$$\Delta T_{max} - \Delta T_{max}(H = 0) = P\Delta t/(c\rho). \qquad (6)$$

when dynamic equilibrium is established.

Figure 2c shows the dependence of the maximum temperature increment on the squared microwave field amplitude. The dependence is linear, which is consistent with Eq. (4). Figure 2d shows an approximation of the dependence of $\Delta T_{max} - \Delta T_{max}(H = 0)$ on field H according to Eqs. (4)–(6) at the fitting parameters given in Table 1. The obtained parameters (particle size, magnetization, and microwave field amplitude) are consistent with the experiment.

Table 1. Fitting parameters

M, G	d, nm	T, K	γ, Hz Oe^{-1}	f, GHz	ξ	h, Oe
17	5.5	293	1.76×10^7	8.9	0.015	2

CONCLUSIONS

Ferrihydrite nanoparticles were synthesized biogenically. The magnetic field dependence of magnetization was measured, and the value of magnetization was found to be 1.78 emu g^{-1} (at $H = 15$ kOe). The temperature dependences of FMR resonance field H_{res} and linewidth ΔH were measured. An $\Delta H(T)$ minimum was observed at a temperature of $T = 350$ K. The temporal dependences of particle temperature were measured upon pumping by a microwave field in a dc magnetic field. The strongest heating was observed under conditions of the resonant absorption of microwave energy. Our experimental results are consistent with the theoretical dependences of the absorbed power of the microwave field for isotropic superparamagnetic systems [4].

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ETHICS APPROVAL AND CONSENT TO PARTICIPATE

This work does not contain any studies involving human and animal subjects.

CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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