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Mechanism of the Formation of an Uncompensated Magnetic Moment in Bacterial Ferrihydrite Nanoparticles

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The magnetic properties of antiferromagnetic nanoparticles of $FeOOH \cdot nH_2O$ with sizes of 3–7 nm, which are products of vital functions of *Klebsiella oxytoca* bacteria, have been studied. Particles exhibit a superparamagnetic behavior. The characteristic blocking temperature is 23 K. Analysis of the magnetization curves shows that the mechanism of the formation of the uncompensated magnetic moment of particles is the random decompensation of magnetic moments of Fe^{3+} ions both on the surface and in the bulk of the antiferromagnetic particle. In this mechanism, the exchange coupling between the uncompensated magnetic moment of the particle and its antiferromagnetic "core" is implemented. It has been found that the temperature dependence of the uncompensated magnetic moment has the form $1 - \text{const}\, T^2$.

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INTRODUCTION

Antiferromagnetic nanoparticles based on ferrihydrite with the general formula $FeOOH \cdot nH_2O$ have attracted great attention in recent years [1–16] because of unusual magnetic properties of these nanoparticles, which are primarily manifested in the existence of the uncompensated magnetic moment of such particles. The understanding of the mechanism of the appearance of the uncompensated magnetic moment in small antiferromagnetic particles is of fundamental importance. In addition, this understanding is important for the possibility of the medical application of antiferromagnetic particles as carriers for the targeted transport of medical products [17].

Horse spleen ferritin is the most studied and, for this reason, is a commercial product. The antiferromagnetically ordered core of ferritin is inside a protein shell with the outer and inner diameters of 12 and 5–8 nm, respectively. This ensures a nanosize of antiferromagnetic ferritin particles with 2000–3000 Fe^{3+} ions. Owing to the existence of the uncompensated magnetic moment, such particles have a superparamagnetic behavior near room temperature and, at low temperatures, exhibit the features inherent in magnetic nanoparticles: the existence of the blocking temperature T_B, the hysteresis behavior of the magnetization, and the relaxation of the magnetic moment (below T_B).

In addition to commercial ferritin, ferrihydrite nanoparticles can be obtained as the products of vital functions of bacteria. It was previously shown that *Klebsiella oxytoca* bacteria in the process of cultivation synthesize ferrihydrite particles close in their structure to ferritin [18–20]. The aim of this work is to study the magnetic properties of these nanoparticles. Using the results of this study, we propose a model of the magnetic state in ferrihydrite nanoparticles of a bacterial origin.

EXPERIMENT

The *Klebsiella oxytoca* strain used in this work was separated from the sapropel of the Borovoe Lake, Krasnoyarsk region. Microorganisms were inoculated into an agar medium and were grown under anaerobic conditions. After multiple ultrasonic processing of bacterial sediments, centrifugation, and washing, a stable sol of nanoparticles in an aqueous solution was fabricated and was then dried. The resulting magnetic nanoparticles were studied. The magnetic properties of dried bacterial sediments for which the blocking temperature characteristic of magnetic nanoparticles was not detected were studied in [21].

The magnetic measurements were performed with a vibration magnetometer [22]. The powder under study was fixed in a measuring capsule in paraffin. The mass of the powder was 12.2 mg. The magnetic measurement data were corrected taking into account the diamagnetic signal from the capsule with paraffin. The zero-field cooling (ZFC) and field cooling (FC) regimes were used.

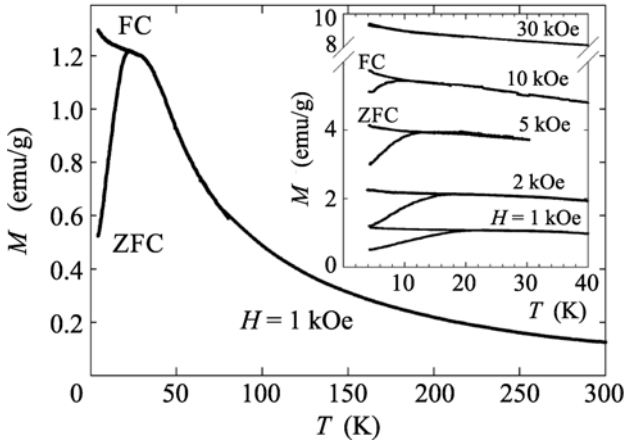

Fig. 1. Temperature dependences (FC and ZFC) of the magnetic moment of the sample under study in the field $H = 1$ kOe. The inset shows similar measurements at different H values in the region of low temperatures.

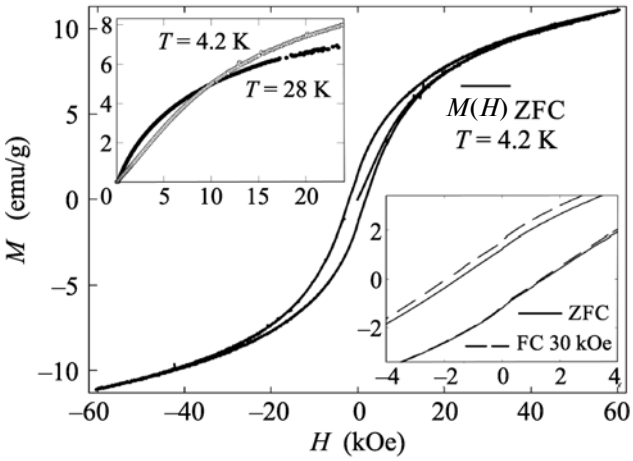

Fig. 2. Hysteresis dependence $M(H)$ at $T = 4.2$ K. The upper inset shows the initial magnetization curves at the indicated temperatures. The lower inset shows the low-field segments of hysteresis dependences $M(H)$ at $T = 4.2$ K after ZFC and FC from $T = 150$ K.

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependences of the magnetic moment in the field $H = 1$ kOe measured under the ZFC and FC conditions. The $M(T)$ dependence measured after ZFC has a maximum at $T \approx 23$ K. The $M(T)$ dependences obtained under the ZFC and FC conditions at this temperature are different. The inset in Fig. 1 shows the ZFC and FC dependences for various strengths of the external field. An increase in the field to ~10 kOe shifts the position of the maximum of the $M(T)$ dependence measured under the ZFC conditions. The $M(T)$ dependences obtained under the ZFC and FC conditions near the maximum are also different. The $M(T)$ dependence for the external field $H = 30$ kOe has no maximum and the temperature of the irreversible behavior of the $M(T)$ dependences decreases to about 7 K. The described behavior of the $M(T)$ dependences is certainly interpreted as characteristic of superparamagnetic systems with the blocking temperature $T_B \approx 23$ K (at $H = 1$ kOe). It is noteworthy that the $M(T)$ dependence above T_B (up to about 40 K) varies slightly. This can be attributed to the difference in the magnetic moment of particles or effective magnetic anisotropy.

Below T_B, the dependence of the magnetic moment on the external field is hysteretic (see Fig. 2). This is typical of superparamagnetic particles, including ferrihydrite and ferritin nanoparticles [1, 3, 5, 7, 8, 13]. Figure 2 shows the $M(H)$ dependence. The coercive force at $T = 4.2$ K in the field range of ±60 kOe is about 1.4 kOe. It is believed [3, 13] that the hysteresis of the $M(H)$ dependence below T_B is due to the effective magnetic anisotropy of particles. This is likely valid for the system of ferrihydrite nanoparticles under study in view of the relative positions of the initial segments of the magnetization curves at $T = 4.2$ and 28 K (hysteresis at $T = 28$ K is almost absent) shown in the upper inset in Fig. 2. The $M(H)$ dependence for fields below 10 kOe at $T = 28$ K is above the $M(H)$ dependence at $T = 4.2$ K, whereas these dependences for higher fields are standard (the magnetic moment decreases with an increase in T).

The $M(H)$ dependences measured at various temperatures above T_B are shown in Fig. 3. The magnetic moment increases quite rapidly for low fields and increases almost linearly for fairly high fields. For this reason, the data can be described by the superposition of the Langevin function (superparamagnetic behavior) and a linear function of the field.

Indeed, when describing the magnetization curves of systems of such ferritin nanoparticles, it is usually assumed that the magnetic moment is determined by the superparamagnetic behavior of the magnetic

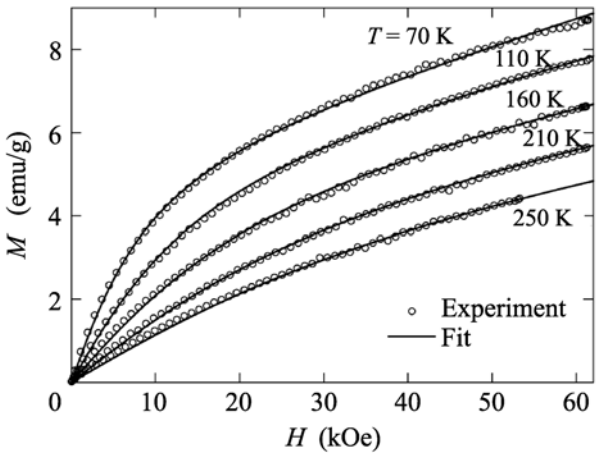

Fig. 3. Isotherms of the magnetization curves at the indicated temperatures: experimental points in comparison with the best fit by Eq. (2).

moment formed by uncompensated spins of the antiferromagnetic particle and by the contribution $\chi_{AF}H$ corresponding to the angularity of the sublattices of the antiferromagnetic core of the particle (here, χ_{AF} is the magnetic susceptibility of the core of antiferromagnetic particles) [3–6, 10, 14].

According to the above consideration and taking into account the distribution of the magnetic moments of particles μ_P, the $M(H)$ dependences can be described by the expression

$$M(H) = N\int_{\mu_{min}}^{\mu_{max}} L(\mu_P, H) f(\mu_P)\mu_P d\mu_P + \chi_{AF}H, \quad (1)$$

where $f(\mu_P)$ is the distribution function of the magnetic moments of the particles. To process the experimental $M(H)$ dependences, we used the log-normal distribution $f(\mu_P) = [\mu_P s(2\pi)^{1/2}]^{-1}\exp\{-[\ln(\mu_P/n)]^2/2s^2\}$, where $\langle\mu_P\rangle = n\exp(s^2)$ is the average magnetic moment of the particle and s is the standard deviation of $\ln(\mu_P)$. The average magnetic moment of the particle $\langle\mu_P\rangle$ and χ_{AF} at various temperatures were varied at fitting. The standard deviation $s \approx 0.2$ and N (the number of particles in 1 g of the powder) remained unchanged. The resulting fits are shown in Fig. 3 by solid lines. It can be seen that the fits obtained within this approach are in good agreement with the experimental points. It is worth noting that, disregarding the distribution function $f(\mu_P)$, the fitting parameters differ by no more than 10% from the values obtained by Eq. (1). However, a difference between the experimental points and fitting curves is observed below 10 kOe.

The fitting parameters $\langle\mu_P\rangle$ and χ_{AF} obtained when processing the experimental $M(H)$ dependences are shown in Fig. 4 as functions of the temperature. The temperature dependence of χ_{AF} is decreasing. This behavior was observed in most studies of the magnetic properties of ferrihydrite and ferritin nanoparticles [3–6, 9, 11].

The authors of [5, 6] proposed to determine the Néel temperature T_N of antiferromagnetic particles by extrapolating the $\chi_{AF}(T)$ dependence at high temperatures to $\chi_{AF}(T) = 0$. The linear extrapolation of the data presented in Fig. 4 gives a value of about 450 K, which is close to similar values obtained in [5, 6] for ferritin.

The temperature dependence of $\langle\mu_P\rangle$ is well described by the power-law expression

$$\langle\mu_P\rangle(T) \sim (1 - \text{const}\,T^2), \quad (2)$$

which is illustrated in the inset in Fig. 4. A similar dependence was observed for ferritin nanoparticles in [5, 6]. It is interpreted within the theory of spin waves in antiferromagnets [23]. For this reason, the T_N value for antiferromagnetic particles can be estimated by

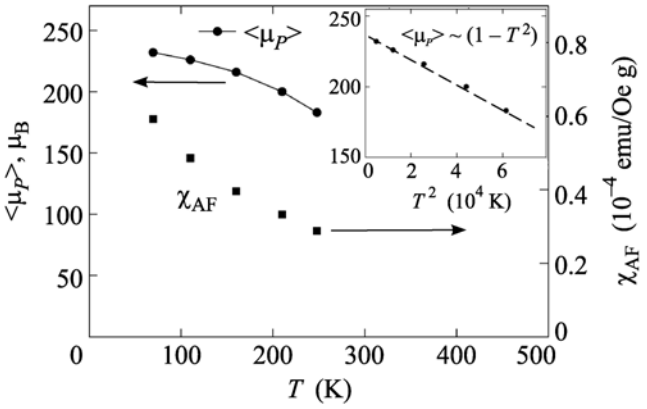

Fig. 4. (Left scale) Average magnetic moment of the particle $\langle\mu_P\rangle$ and (right scale) magnetic susceptibility of the core of antiferromagnetic particles χ_{AF} obtained from the conditions of the best agreement between the experimental and fitting curves $M(H)$ in Fig. 2. The inset shows $\langle\mu_P\rangle$ versus T^2 illustrating the behavior corresponding to Eq. (2).

extrapolating Eq. (2) to $\langle\mu_P\rangle = 0$. The temperature dependences of the uncompensated magnetic moment for the nanoparticles under investigation and ferritin nanoparticle are similar to each other. At the same time, to understand the temperature dependence $\langle\mu_P\rangle(T)$, it is reasonable to study particles with different sizes. This will be the subject of future investigations. It is noteworthy that the extrapolation of $\langle\mu_P\rangle(T)$ to $\langle\mu_P\rangle = 0$ gives a value of 520 K.

At the same time, the knowledge of the $\langle\mu_P\rangle(T)$ dependence makes it possible to reliably extrapolate the low-temperature data to $\langle\mu_P\rangle(T=0)$. This extrapolation yields $\langle\mu_P\rangle(T=0) \approx 235\mu_B$. The values $\mu_{eff} \sim (200–400)\mu_B$ were obtained for ferritin nanoparticles in [3–7, 10]. At the magnetic moment of 5 μ_B of the Fe^{3+} ion, the number of iron ions whose spins are uncompensated is $N_{un} \approx 50$. This is certainly valid only for the case of the ideal "ferromagnetic" orientation of uncompensated magnetic moments of Fe^{3+} ions.

Analyzing the studies of the morphology and structures nanoparticles produced by *Klebsiella oxytoca* bacteria performed with various methods [24], we can conclude that these particles are long cylinders with the characteristic sizes of about 3 and 6–7 nm. At an average distance of 3 Å between iron ions in ferrihydrite [7], the number of Fe^{3+} ions in a nanoparticle is estimated as $N \sim 2000–2500$. According to the Néel hypothesis [25], the magnetic moment of a small antiferromagnetic particle induced by random violation of the spin order on the surface is proportional to $N^{1/3}$, i.e., $\mu_P = N_{un}\mu_{at} = N^{1/3}\mu_{at}$ (where μ_{at} is the magnetic moment of the atom). If violations of the spin order occur both on the surface and in the bulk of the parti-

cle, the magnetic moment of the antiferromagnetic particle is proportional to $N^{1/2}$, i.e., $\mu_P = N^{1/2}\mu_{at}$. The value $N_{un} \approx 50$ obtained above corresponds to the latter case ($N^{1/2} \sim 45$–50). Thus, the analysis of the magnetization curves and previous estimates of the sizes of ferrihydrite nanoparticles shows that the magnetic moment in particles under study is due to uncompensated iron atoms located both on the surface and in the bulk.

It is known that the magnetic hysteresis loop for nanoparticles simultaneously having the antiferromagnetic order and uncompensated magnetic moment is shifted upon cooling in the external field [3, 7, 13, 14]. A similar behavior is observed for bacterial ferrihydrite nanoparticles. The lower inset in Fig. 2 shows the low-field segments of hysteretic $M(H)$ dependences at $T = 4.2$ K measured in fields up to ±30 kOe after zero-field cooling and field cooling from a temperature of 150 K (which is certainly higher than T_B). As can be seen, the bias field under the indicated conditions is approximately 400 Oe. The reasons for such a behavior can be different (e.g., the exchange interaction of the uncompensated magnetic moment with the antiferromagnetic core [7] or with regions of the particle [14], the effective magnetic anisotropy of particles [13], and the spin-glass behavior of the surface magnetically active atoms of the particle [3]).

CONCLUSIONS

To conclude, analyzing the previous experimental data for ferritin [19, 20, 24] and studies of the magnetic properties of biological ferrihydrite, we can propose the following model of the magnetic state in ferrihydrite nanoparticles under study. The magnetic moments of Fe^{3+} ions in the bulk of nanoparticles are antiferromagnetically ordered. The particles have the effective magnetic moment, which is responsible for their superparamagnetic behavior with the characteristic blocking temperature $T_B > 23$ K. The average magnetic moment of particles $\langle \mu_P \rangle \sim 250\mu_B$ is consistent with the Néel hypothesis of the random decompensation of the magnetic moments of magnetically active ions (Fe^{3+}) located both on the surface and in the bulk of a small antiferromagnetic particle. The temperature dependence of the uncompensated magnetic moment of the particles follows a power law $1 - T^2$. The experiment indicates the exchange shift of the hysteresis loop in the case of cooling in the external magnetic field from a temperature above the blocking temperature.

All revealed features indicate that the behavior and physical mechanisms of the formation of the magnetic moment in the small antiferromagnetic particles of bacterial ferrihydrite under study are similar to those in ferritin particles.

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