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Magnetic resonance of Fe_3O_4 nanoparticles with their different amount in the ensemble

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Ferromagnetic resonance was studied using magnetite nanoparticles (Fe_3O_4) obtained by cryochemical synthesis. The initial nanoparticle suspension was prepared in butyl alcohol and subsequently diluted to achieve different Fe_3O_4 concentrations. The resonance line width, the area under the resonance absorption line, absorption intensity and the value of the resonant magnetic field at a fixed frequency were determined. A quadratic dependence of the dipole-dipole interaction on the change in the total mass of magnetic nanoparticles in the ensemble was established. The value of the effective magnetic field was determined.
Keywords: nanoparticle concentration, magnetic resonance, nanoparticles, magnetite, ultra-high frequencies.

Магнітний резонанс у наночастинках Fe_3O_4 за їхньої різної кількості в ансамблі.
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Дослідження методом феромагнітного резонансу було проведено з використанням наночастинок магнетиту (Fe_3O_4), одержаних кріохімічним синтезом. Вихідна суспензія наночастинок була приготовлена в бутиловому спирті з подальшим розведенням для варіювання концентрації. Визначено ширину резонансної лінії, її інтегральну площину та інтенсивність поглинання, а також величину резонансного магнітного поля на заданій частоті. Визначено, що залежність диполь-дипольної взаємодії через зміну загальної маси наночастинок у ансамблі має квадратичний характер. Визначено значення ефективного магнітного поля наночастинок.

1. Introduction

Magnetic nanoparticles have attracted great interest in medicine [1-2]. Recently, a technique for targeted delivery which is based on a combination of magnetic nanoparticles with a medical drug has been developed [3-5]. However, this technique has not been yet implemented in medical practice due to a number of unsolved problems. One of these problems is the impossibility of determining the concentration of nanoparticles and their magnetic state inside the organism. The efficiency of nanoparticles could depend on their concentration in direct proportion. However, this is not the case. Without dwelling on toxicological aspects, it should be noted that an increase in the concentration of magnetic nanoparticles in a constant volume obviously leads to an increase of magnetic dipole-dipole interaction between nanoparticles as they come closer together [3]. This leads to the significant change in their magnetic state in the ensemble by changing the effective magnetic field. The dipole-dipole interaction between magnetic nanoparticles is well described in theoretical [4-6] and experimental [7, 8] works. Unfortunately, a complete theoretical model of the dipole-dipole interaction between

nanoparticles has not been developed due to the difficulty of taking into account all physical parameters of the nanoparticles, which are randomly located in the ensemble. A deeper analysis of the magnetic interactions between nanoparticles is needed. Experimental studies of magnetic nanoparticles using the method of radio spectroscopy in the region of ultra-high frequencies make it possible to determine the contribution of dipole-dipole interaction to the effective magnetic field H_{eff} of nanoparticles. Thus, we can define the criterion under which this interaction is predominant in H_{eff}. This becomes possible with control of the variability of the amount of nanoparticles in the ensemble. This can be achieved, for example, by diluting nanoparticles in liquids to obtain their different concentrations in suspensions.

The aim of this work is to study the magnetic dipole-dipole interaction between chaotically located nanoparticles in suspensions at different concentrations using the magnetic resonance method. Magnetite nanoparticles (Fe_3O_4) obtained by the cryochemical synthesis method [9] were chosen as the material under study. Their advantage is a small spread of sizes [10] and high thermal stability of magnetic properties [11].

2. Theory

The effective magnetic field (under normal conditions) is mainly determined by magnetic crystalline anisotropy, surface anisotropy, and shape anisotropy of nanoparticles in the case where the dipole-dipole interaction between nanoparticles is negligible [12, 13]. Typically, nanoparticles are located randomly in space and their anisotropy axes are located in different directions. Due to this disorder, the scalar value of the effective magnetic field of the nanoparticle ensemble has some spread. Indeed, the width of the magnetic resonance line is significantly larger than the same width for a single nanosized particle. The magnetic resonance modeling of a single nanoparticle allows estimating the spread of the effective magnetic field scalar value [4]. Firstly, we assume that the precession of magnetization is uniform throughout the volume of a single nanoparticle, i.e. without taking into account the contribution of anisotropy of the shape, surface, direction of magnetization axes in the crystal into the effective field H_{eff}, which is included in the Landau-Lifshitz equation [14] as follows:

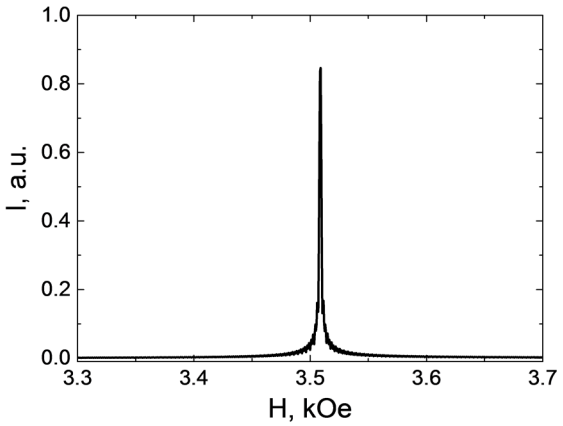

Fig. 1. Numerically simulated magnetic resonance line for a single nanoparticle at 10 GHz without taking into account anisotropy fields

$$\frac{d\mathbf{M}}{dt} = -\gamma\left[\mathbf{M},\mathbf{H}_{\mathbf{eff}}\right] - \alpha\left(\frac{\gamma}{M}\right)\cdot\left[\mathbf{M},\left[\mathbf{M},\mathbf{H}_{\mathbf{eff}}\right]\right], \quad (1)$$

where M and H_{eff} are magnetization and effective magnetic field vectors, α is a damping parameter (determined by the property of the magnet), γ is the effective gyromagnetic ratio.

It should be noted here that the scalar effective magnetic field H_{eff} includes the external magnetic field with the value H. Having reached the resonance value $H=H_{res}$, the absorption acquires its maximum (peak) value. The solution of equation (1) also allows us to determine the shape of magnetic resonance line for a single nanoparticle at a certain linear frequency f. So, the numerical simulation of magnetic resonance in the region of fields H, where peak absorption is observed, we performed using the model described in the article [15]. The physical parameters for the numerical simulation were obtained from the work [11]. Our numerical simulation results of the magnetic resonance line for one nanoparticle are shown in Fig. 1. The simulated magnetic resonance line can be conveniently described by the Lorentz function.

Fig. 1 shows that the width of the magnetic resonance line of a single nanoparticle without taking into account the anisotropy fields is about 2 Oe. Based on the research data of [10, 11], it is clear that the experimental line width for the ensemble of nanoparticles is more than two orders of magnitude larger than the line width of a single magnetic nanoparticle (Fig. 1). Undoubtedly, this indicates both the presence of anisotropy, which must be taken into account in the effective field H_{eff}, and the presence of dipole-dipole interaction between nanoparticles. The contribution of these factors

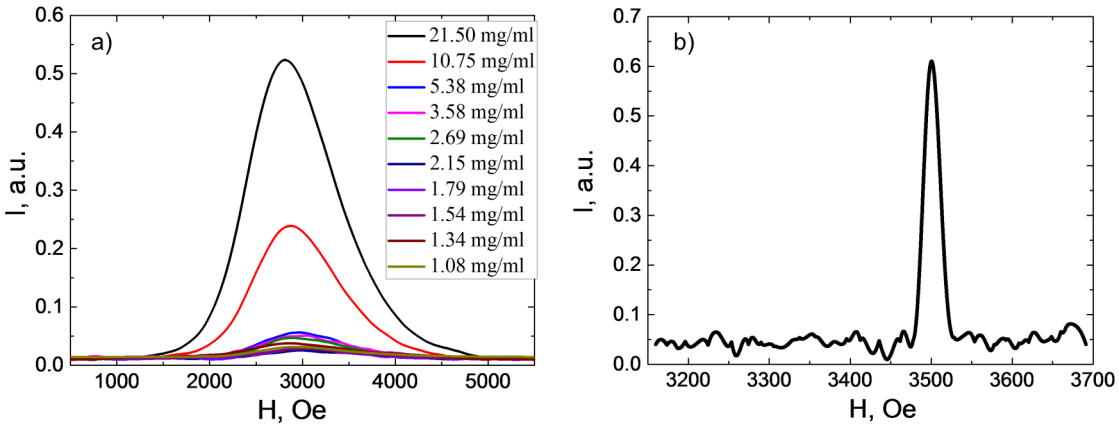

Fig. 2. Resonance absorption lines of a) Fe_3O_4 nanoparticles of different concentrations by dilution in butyl alcohol and b) 2,2-diphenyl-1-picrylhydrazyl

can be estimated from the shape, area and intensity of the magnetic resonance lines [16].

The area under the resonance absorption line A can be determined using numerical calculation programs for processing spectral data or by the formula [16]:

$$A = \sum_{j=1}^{N} I_j \left(H_j - H_{j-1} \right), \qquad (2)$$

where I_j is the jth value of intensity along the y-axis at the field value H_j. Expression (2) is suitable for describing magnetic resonance in an ensemble of N nanoparticles. The area and intensity of the magnetic resonance line is directly proportional to the number of magnetic nanoparticles [16]. In its turn, it is obvious that the mass of nanoparticles in the studied sample m is directly proportional to the number of nanoparticles N in it (i.e. $m \sim N$).

An increase in the number of nanoparticles in a constant volume leads to an increase in the dipole-dipole interaction between nanoparticles and, as a consequence, to the formation of conglomerates, which are similar in their magnetic properties to a polycrystal [3, 4, 17]. Therefore, the magnetic resonance line becomes wider due to the additional magnetic energy of interaction. The increase in intensity and area become nonlinear [3].

The magnetic resonance line shape and line width of the entire ensemble of nanoparticles are usually well described by the lognormal distribution of the field value H [10], which usually follows the shape of the lognormal distribution of nanoparticles by their size and number [18]. Thus, the dependence of the number of nanoparticles on their diameter (diameter distribution) can be written as [18]:

$$N = \frac{p}{\Delta p\, d\sqrt{2\pi}} \cdot \exp\left(\frac{-\ln\left(d/l\right)^2}{2\Delta p^2} \right), \qquad (3)$$

where p is the normalization parameter, Δp is the distribution parameter, l is the size parameter, d is the averaged size of a nanoparticle. The order of magnitude of the parameter l is the same as same as when measuring nanoparticles. Taking into account the surface anisotropy field, as described in [10], the magnetic resonance line shape can be expressed as follows:

$$I = \frac{1}{\Delta H_{res}\sqrt{2\pi}} \cdot \exp\left[-\frac{1}{2} \frac{\ln\left(H_{res}/\Delta H_{res}\right)^2}{\Delta H_{res}} \right], \qquad (4)$$

where H_{res} is the resonant value of the field H, ΔH is the distribution parameter related to the width of the magnetic resonance line at its half-height. The magnitude of the field H_{res} is determined by the value of the field H_{eff}. The effective anisotropy coefficient at H_{eff} can be found from the experiment described below.

3. Results and discussion

Magnetic resonance was studied for Fe_3O_4 nanoparticles synthesized by the cryochemical method. A detailed description of the synthesis method can be found in [9]

The nanoparticles were diluted in butyl alcohol with the initial concentration of 21.5 mg/ml and dispersed using an ultrasonic device UZDN-2T for 2 minutes (at an operating frequency of 44 kHz and a power of 1 kW) to destroy possible conglomerates of nanoparticles and create a homogeneous suspension.

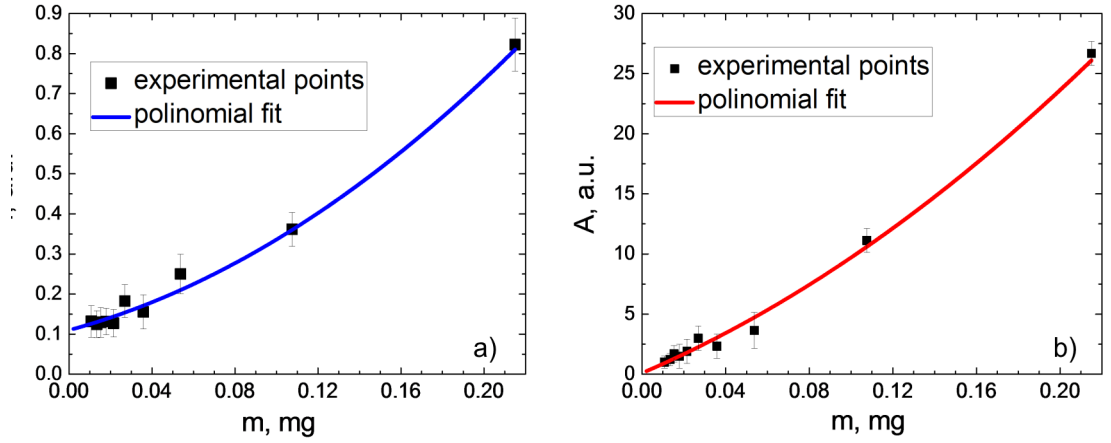

Fig. 3. Dependences of the magnetic resonance line absorption on the total mass of nanoparticles m in the sample: a) intensity I; b) area A

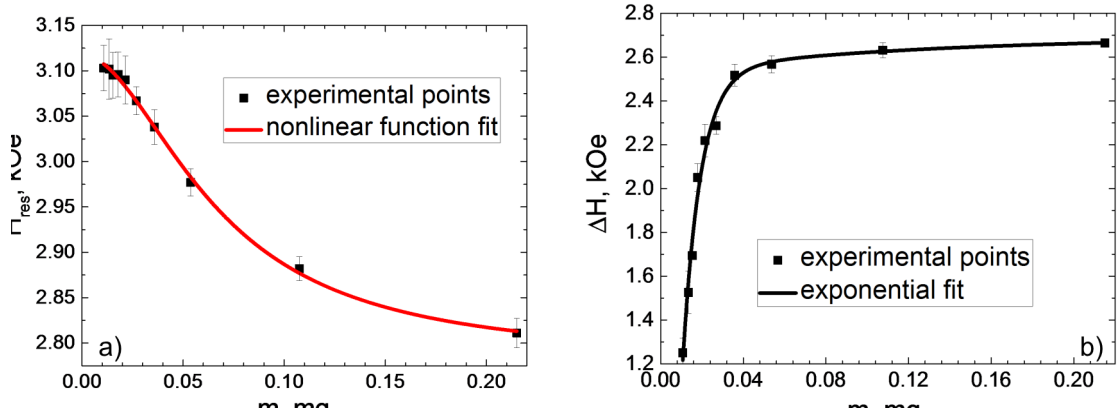

Fig. 4. Dependences on the total mass of nanoparticles m in the sample: a) the magnetic resonance field H_{res} and b) width at half maximum ΔH of resonance absorption lines

A series of 10 samples was prepared from the initial suspension by diluting it with butyl alcohol. The concentration of nanoparticles varied from 1.075 to 21.500 mg/ml. An exact volume of 0.01 ml from each suspension was placed onto a filter paper.

Each sample was investigated by magnetic resonance using the technique described in [10]. The linear resonance frequency was chosen to be 10 GHz (equal to the frequency in the simulation). The study was carried out under normal atmospheric conditions. A cavity resonator with a cross section of 23×10 mm was used. The frequency was set and controlled by a vector network analyzer. The reference sample was 2.2-diphenyl-1-picrylhydrazyl (DPPH) with a known spin concentration. The peak value of the resonance field and the width of the magnetic resonance line of the nanoparticles were controlled by the magnetic resonance line of the DPPH. The experimental magnetic resonance absorption results are shown in Fig. 2.

Fig. 2 shows a clear increase in the microwave absorption intensity I with increasing total mass of nanoparticles in the sample. Also noticeable is an increase in the area A, limited by the resonance line and the asymptote coinciding with the abscissa H. These two values are presented as dependences on the total mass of nanoparticles in the sample (Fig. 3).

The graphs in Fig. 3 show the 2nd order polynomial function for the magnetic resonance line intensity I versus the total mass of nanoparticles and the same function for the area A. The linear dependence would be associated with an increase in the number of nanoparticles, namely the number of unpaired spins in the ensemble of magnetic nanoparticles [16]. However, the quadratic dependence indicates the presence of dipole-dipole interaction. It is clear that with increasing concentration of nanoparticles, the distance between nanoparticles decreases and the dipole-dipole interaction between the nanoparticles prevails over other factors (included in H_{eff})

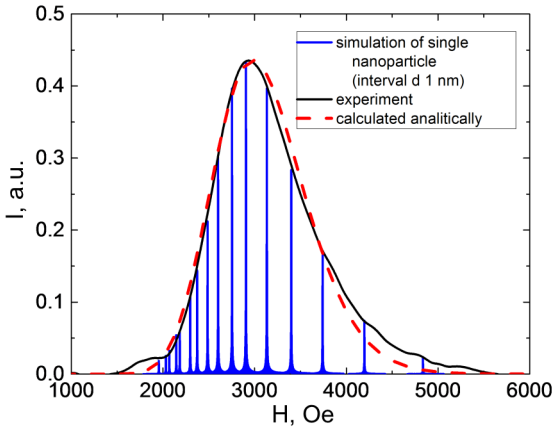

Fig. 5. Experimental magnetic resonance line of nanoparticles (solid line) for m=10.75 μg and calculated according to (5) (dashed line); simulated numerically magnetic resonance lines for nanoparticles of different sizes (with their diameter interval of 1 nm) (blue peaks)

affecting I and A. The dependences observed in Fig. 3 are confirmed by the analysis of the dependencies of the peak values of the resonant field and the width of the magnetic resonance line at half maximum (Fig. 4).

At low concentrations, H_{res} changes insignificantly, since the nanoparticles are in the superparamagnetic state; the magnitude of the resonance field of the nanoparticles tends to the magnitude of the effective magnetic field $|H_{eff} - H|$. The effective magnetic field, as mentioned above, is determined by the factors described, for example, in [12, 13]. A similar phenomenon was confirmed in [10], where nanoparticles were treated with the surfactant Triton-X100, which prevented their agglomeration and reduced the effect of dipole-dipole interaction between the nanoparticles [17]. Analysis of the magnetic resonance lines of the nanoparticles with a total mass of 10.75 μg, when the dipole-dipole interaction is insignificant, showed an effective field H_{eff} = 374 Oe. For the nanoparticles under study, the influence of demagnetizing factors should be minimal, since they have a shape close to spherical [9]. Therefore, demagnetizing factors are negligibly small in H_{eff}.

The graph of the $H_{res}(m)$ dependence has an inflection region (Fig. 4a), which may indicate the presence of a magnetic phase transition of nanoparticles from the superparamagnetic to the ferromagnetic polycrystalline state [18]. Due to the increase in dipole-dipole interaction the line width ΔH increases. The dependence $\Delta H(m)$ is exponential.

A comparative analysis of the theoretical and experimental magnetic resonance line was carried out. Fig. 5 shows the results of numerical modeling of magnetic resonance in nanoparticles of different diameters to demonstrate the influence of surface anisotropy of the nanoparticles. In the numerical modeling, the sizes of nanoparticles were chosen in the range of 5-20 nm with a step of 1 nm for clarity. However, it is worth mentioning that in a physical system, nanoparticles have a continuous set of size values, so the experimental line of magnetic resonance is continuous.

The results presented in Fig. 5 show a good agreement of the experimental magnetic resonance line with the calculated one. The results of the numerical calculations made it possible, taking into account the experimental data and the results presented in [8], to obtain the effective anisotropy constant K_{eff} of the total effect of magnetic crystalline anisotropy, surface anisotropy and shape anisotropy fields. It amounted to 3.8×10^6 erg/cm^3.

4. Conclusions

The study of the magnetic resonance spectra of Fe_3O_4 nanoparticles prepared by cryochemical synthesis showed that the intensity of the ferromagnetic resonance line and its area (limited by the resonance line and the asymptote coinciding with the abscissa axis H) are described by a second-order polynomial function. The linear dependence is explained by the increase in the number of nanoparticles (increase in their total mass). The obtained quadratic dependence can be explained by the strengthening of the dipole-dipole interaction between nanoparticles. In the case of low concentrations of magnetic nanoparticles, when the dipole-dipole interaction can be neglected, the magnitude of the H_{eff} field is 374 Oe.

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