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Magnetic and magneto-optical properties of Fe_3O_4 and $NiFe_2O_4$ nanoparticles

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In this paper, we present study of the measurement peculiarities of magnetic Fe_3O_4 and $NiFe_2O_4$ nanoparticles characteristics. The nanoparticles possess ferromagnetic properties. The aim of the work was to determine the magnetic parameters of such nanoparticles and to investigate influence of magnetic field and interaction between individual nanoparticles on the value of their magnetic characteristics. Atom force and magnetic microscopy, method of magnetic susceptibility measuring, magneto-optical technique and method of ferromagnetic resonance were used in the research.

Исследованы особенности измерения характеристик магнитных наночастиц Fe_3O_4 и $NiFe_2O_4$, обладающих ферромагнитными свойствами. Цель работы – определение магнитных параметров таких наночастиц, исследование влияния магнитного поля, влияние взаимодействия между отдельными наночастицами на величину магнитных характеристик. Использованы методика атомной силовой, магнитной микроскопии, методика измерения магнитной восприимчивости, магнитооптическая методика и метод ферромагнитного резонанса.

Магнітні ш магнітооптичні характеристики наночастинок Fe_3O_4 і $NiFe_2O_4$. *Н.Н. Крупа, І.В.Шарай*

Досліджено особливості вимірювання характеристик магнітних наночастинок Fe_3O_4 і $NiFe_2O_4$, що мають феромагнітні властивості. Мета роботи – визначення магнітних параметрів таких наночастинок, дослідження впливу магнітного поля, вплив взаємодії між окремими наночастинками на величину магнітних характеристик. Використано методики атомно- силової, магнітної мікроскопії, вимірювання магнітної сприйнятливості, магнітооптичну методику і метод феромагнітного резонансу.

1. Introduction

Nanoparticles that have magnetic properties are of considerable interest and they are applied in many fields of science and medicine. Recently, much attention is paid to study of the magnetic nanoparticles due to their remarkable properties, that make them attractive in terms of both fundamental research and for potential use in the various technological fields. For example, the particles of magnetic oxides of iron (maghemite — $NiFe_2O_4$ and magnetite Fe_3O_4) find application in such areas as development the separation of waste, the targeted delivery of the drugs, the hypothermic treatment of cancer cells, the magnetic media, photonic crystals, and others. In addition, the magnetic nanoparticles have unusual characteristics, that make them interesting in scientific terms and cause the wide interest in study of their fundamental physical properties. This paper presents the results of measurements of geometric, magnetic and magneto-optical characteristics of the magnetic nanoparticles Fe_3O_4 and $NiFe_2O_4$, as well as influence of the constant magnetic field on the magnetic properties of these particles was studied.

2. Experimental

Estimation of the nanoparticles (Fe_3O_4 and $NiFe_2O_4$) sizes was performed by means of scanning probe microscope Solver PRO-M. During measurement the "two pass" technique was used which consists of the microscopy of two types: atomic-force microscopy (AFM) and magnetic-force microscopy (MFM). Semicontact and magnetic scan regimes were used. It should be noted, that AFM possible fairly accurately estimates the height of the particles separately located. But visible horizontal dimensions of the particles, whose radius is comparable with the radius of curvature of the top of the needle, can be significantly more than real ones because of the known convolution effect of the tip-sample. Therefore for estimation of the nanoparticles size the height values of the AFM image were taken into account. The values were processed by Grain Analysis v2.2 (NT-MDT) program [1].

In Fig. 1 optical setup is shown which was used to study the Faraday effect. Optical part of the setup comprises: a source of light — a halogen lamp, a polarizer and the analyzer (the second of which is located at an angle of 45° to the plane of polarization of the polarizer) and a glass cell with the sample. Photomultiplier as a photodetector of infrared and visible light range was used.

Photocurrent registration was performed by analog to digital converter ICP-CON I7017 with subsequent digital processing of the data arrays. To create the saturating magnetic field with intensity 0.265 T the electromagnet was used, the field direction was switched by relay circuit. In the work Fe_3O_4 and $NiFe_2O_4$ nanoparticles were investigated. Samples for observation of the Faraday effect with concentrations n_1 and n_2 (n_2 — second sample concentration is approximately half of the concentration n_1) were prepared. The main idea of the experiment was to reduce the nanoparticles concentration to create the possibility to perform calculations for a single nanoparticle. Studies in the solid (the nanoparticles powder) and liquid (solutions in glycerol) environments were performed. Cuvette containing the sample was placed between the poles of a magnet. The Faraday effect in these samples in the infrared and the visible light was observed.

Ferromagnetic resonance spectra of the nanoparticles of Fe_3O_4 and $NiFe_2O_4$ were obtained using a Bruker Elexsys E-500 with an operating frequency range x range of 9,877 GHz at the room temperature (294 K) in magnetic field $H = 0 \div 7000$ Oe. The sample was placed at the antinode of the magnetic component of microwave field. The resonator quality factor in the measurement process was controlled (for Fe_3O_4 nanoparticles: $Q = 5800$, $NiFe_2O_4$:$Q = 5300$). Microwave radiation power in the resonator was 0.2 mW. In the magnetic resonance spectra of $NiFe_2O_4$ nanoparticles we observed a broad line of the Gaussian shape due to the set of resonance frequencies that depend on the heterogeneity of the particle size and shape.

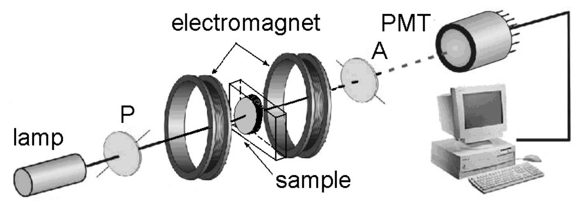

Fig. 1. The optical device.

3. Results and discussion

Scanning Probe Microscopy. For stimation of the particles size we used the AFM height value, that processed by the program Grain Analysis v2.2 (NT-MDT). Histogram of the particle distribution in height has been created.

Magnetic susceptibility determination for Fe_3O_4 and $NiFe_2O_4$ powders. The coaxial circuit consisted of a solenoid (a coil and a condenser) was used to measure the nanoparticles magnetic susceptibility by the resonance method [2]. The measuring contour consists of a frameless coil (external diameter ∅8 mm, internal diameter ∅6 mm) that has been made of ∅0.5 mm copper wire. The magnetic nanoparticles were located in the middle of the coil. Two types (Fe_2O_3 and Fe_3O_4) of the nanoparticles were studied. Magnetic properties of the nanoparticles were estimated by measurement of the contour resonant frequency of the both coils: with the particles and the empty one.

Inductance of a solenoid, filled with air $\mu = 1$, was determined by the relation:

$$L_0 = k\mu_0 N^2 \frac{S}{l}. \quad (1)$$

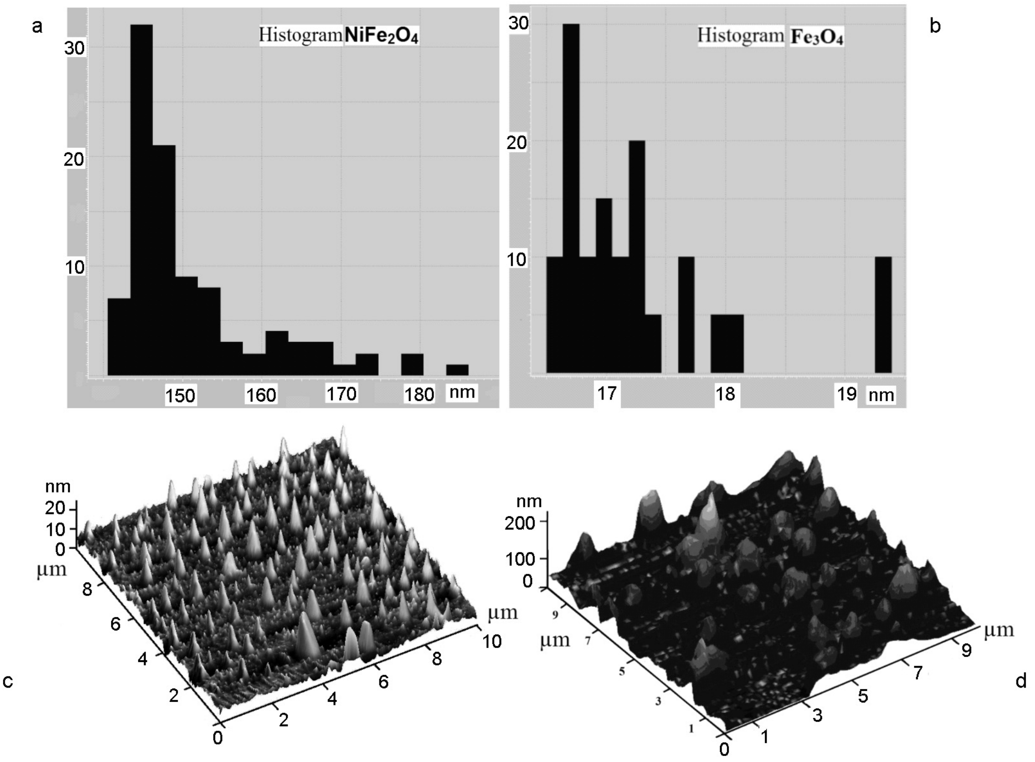

Fig. 2. a) Histogram of distribution in height for magnetic nanoparticles $NiFe_2O_4$, b) histogram of distribution in height for magnetic nanoparticles Fe_3O_4, c) 3d AFM images of $NiFe_2O_4$ magnetic nanoparticles, d) 3d AFM images of Fe_3O_4 magnetic nanoparticles.

Inductance of a solenoid with magnetic powder — $L = k\mu\mu_0 N^2 S/l$, then the change of inductance:

$$\Delta L = L - L_0 = k\mu_0 N^2 \frac{S}{l}(\mu - 1) = \chi\mu_0 N^2 \frac{S}{l} k, \quad (2)$$

when χ — magnetic susceptibility of a powder, which was placed in a coil. The resonant frequency of the circuit is determined by the relation: $f = 1/2\pi\sqrt{LC}$. Shift of the resonance frequency at the entry of the magnetic powder to the plane of the solenoid is:

$$|\Delta f| = |f - f_0| = \frac{1}{2\pi\sqrt{C}\left(\frac{1}{\sqrt{L_0 + \Delta L}} - \frac{1}{\sqrt{L_0}}\right)} =$$

$$= f_0 \left|\frac{\Delta L}{2L_0}\right| = f_0 \frac{\chi\mu_0 N^2 \frac{S}{L} k}{2\mu_0 N^2 \frac{S}{l} k} = \frac{f_0 \chi}{2}.$$

From this relation, the magnetic susceptibility of the powder is the following:

$$\chi = \frac{2\Delta f}{f_0}. \quad (3)$$

Magnetic field influence on the value of the magnetic susceptibility of Fe_3O_4 *and* $NiFe_2O_4$ *powders.* The measurements were

Table. Parameters of ferromagnetic resonance spectra of the nanoparticles

The sample	χ, 1/kg	size, nm	g-factor	The line width ΔH_{pp}, Oe	The peak position of the absorption signal, Oe	
					The main peak	Additional peak
Fe_3O_4	$3 \cdot 10^{-2}$	16–20	2.2827	2701	2926	–
$NiFe_2O_4$	$2 \cdot 10^{-3}$	140–160	3.4235	1530	2044	910

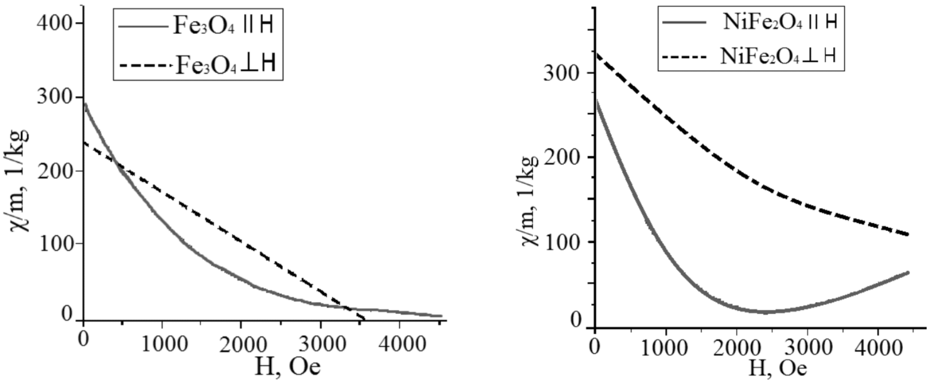

Fig. 3. Results of the measurements of magnetic susceptibility of Fe_3O_4 and $NiFe_2O_4$ nanoparticles depending on the direction and intensity of the applied constant magnetic field.

carried out with application of magnetic field. The measuring coil with magnetic nanoparticles was placed between the electromagnet poles. The field was applied both along the coil axis and perpendicularly to the coil axis, i.e. perpendicularly to the high-frequency measuring field. The results of the field dependence of the magnetic susceptibility of Fe_3O_4 and $NiFe_2O_4$ powders are shown in Fig. 3.

In addition we have established that in static magnetic field the value of the magnetic susceptibility of the investigated nanoparticles χ changes. For nanoparticles $NiFe_2O_4$, when direction of the static magnetic field coincides with the variable measured field the value of χ increases, when the direction of the static magnetic field perpendicular to the direction of the measured variable field, the value of χ reduced. For Fe_3O_4 the χ value decreases as well in parallel and perpendicular to the direction of the static magnetic field and the measured variable field. The received dependence can be possible explained by anisotropy of the magnetic nanoparticles (shape anisotropy or the crystal structure anisotropy). This behavior of the magnetic susceptibility in constant external magnetic field indicates that it is under influence of the magnetic interaction between particles. This effect may be caused by the volume distribution and the inhomogeneous magnetic structure of the nanoparticles, as well as the random orientation of easy axes of magnetization. The external magnetic field influences on the magnetic order. It arranges the magnetic moments of the nanoparticles by rotation of magnetic moments in a single direction. The main problem of the measurement of the magnetic susceptibility by resonance method is that inductance of the coil with the magnetic nanoparticles varies not only due to the contribution of the actual values of the magnetic susceptibility, but also by conductivity increasing. Therefore, to measure using to use this method, the non-conductive magnetic nanoparticles need to be used. Also contribution of the change in conductivity of the coil's inductance should be taken into account [3].

The Faraday effect. Measured spectra of the Faraday effect are shown in Fig. 4. In the study of the Faraday effect the changes in the spectra depending on the nanoparticles concentration were observed. The effect was more significant in the wavelength range of visible light. The maximum value of the Faraday angle observed for $NiFe_2O_4$ nanoparticles in the wavelength range of 550–730 nm for Fe_3O_4 nanoparticles — in the wavelength range of 700–830 nm which can be associated with the contribution of the resonance characteristics in the magneto-optical interaction of magnetic atoms of iron and nickel. Such measurements still need to use the fixed nanoparticles (dry powder or transparent polymer matrix) as even in viscous liquids (glycerol) under the influence of the magnetic field nanoparticles aligned along the field lines to form agglomerates, which affects the measurements accuracy.

Ferromagnetic resonance spectra of nanoparticles Fe_3O_4 *and* $NiFe_2O_4$. In the magnetic resonance spectra of $NiFe_2O_4$ nanoparticles we observed the broad lines of the Gaussian shape by the set of resonance frequencies, which depend on the heterogeneity of the particles sizes and shapes. For Fe_3O_4 nanoparticles the experimental spectra at the room temperature are slightly asymmetrical single lines with the effective *g*-factor of 2.2827 and with the width of 2701 Oe, which is typical for the ferromag-

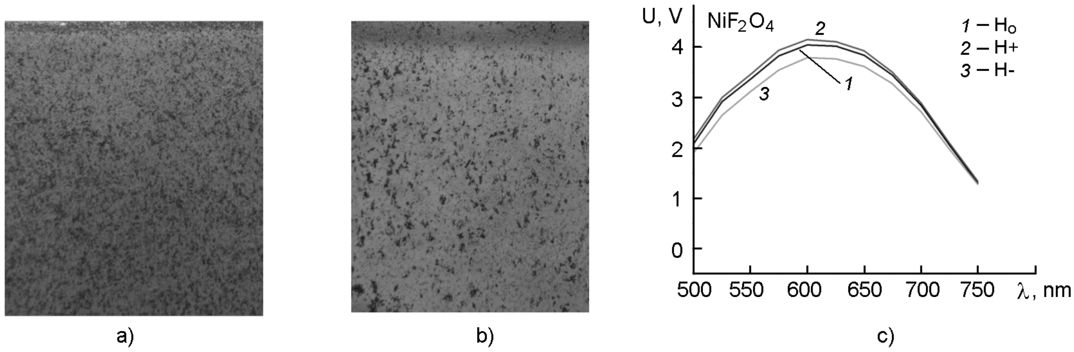

Fig. 4. Nanoparticles in glycerine: a) without magnetic field, b) in magnetic field, c) spectra of the Faraday effect of $NiFe_2O_4$ nanoparticles: without magnetic field — H_0, at magnetic field $H = \pm 2.650$ kOe.

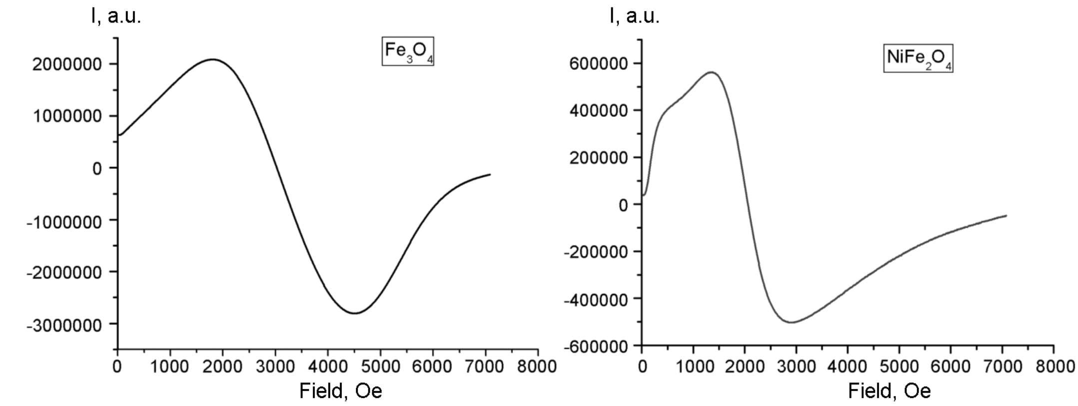

Fig. 5. Ferromagnetic resonance spectra of nanoparticles: a) Fe_3O_4 and b) $NiFe_2O_4$.

netic resonance of spherical nanoparticles. In the case of $NiFe_2O_4$ nanoparticles two magnetic phases are observed, which may indicate that the other iron compounds are presented in the powder in addition to $NiFe_2O_4$ nanoparticles. Consequently, Fe_3O_4 nanoparticles are more homogeneous in composition and sizes than $NiFe_2O_4$ which contain impurities $Ni_xFe_{2-y}O_4$ [4] .

4. Conclusions

The results show that the geometric dimensions were: for nanoparticles Fe_3O_4 — 20–100 nm with a maximum density of the distribution function near 20–40 nm; for nanoparticles $NiFe_2O_4$ — 30–150 nm with a maximum density of the distribution function near 40–60 nm. Magnetic susceptibility of the magnetic nanoparticles is $\chi = \approx 3\cdot 10^{-2}$ for Fe_3O_4 and $\chi = \approx 2\cdot 10^{-3}$ for $NiFe_2O_4$. In addition we have established that the magnetic susceptibility value of the investigated nanoparticles χ changes in static magnetic field. The value of χ increases for $NiFe_2O_4$ nanoparticles, when the direction of the static magnetic field coincides with the direction of measured variable field. In the opposite case, when direction of the static magnetic field is perpendicular to direction of the measured variable field the value of χ reduces. For Fe_3O_4 the value of χ decreases for the both (parallel and perpendicular) directions of the static magnetic field to the measured variable field. The received dependence can be explaineed by anisotropy of the magnetic nanoparticles (shape anisotropy or crystal structure anisotropy).

Faraday effect of the samples of Fe_3O_4 and $NiFe_2O_4$ nanopowders with concentrations of the particles n_1 and n_2 ($n_1 \approx 1/2\ n_2$) showes that the results depend on the powders concentration and the environment in which the measurements were made. Such measurements need to use fixed nanoparticles (dry powder or transparent polymer matrix or in viscous liquids). It is established that under the influence of constant magnetic field the nanoparticles aligne along the field lines forming agglomerates. This behavior is resulting in a change of the magnetic susceptibility, the line shape and position of the FMR spectrum, and the Faraday magneto-optical spectra. Fe_3O_4 nanoparticles are more uniform in composition comparing with the nanoparticles of $NiFe_2O_4$. The structuring of the nanoparticles to form the linear aggregates of the magnetic particles may also lead to appearance of additional lines in the spectrum of FMR. Changes in the nanoparticles concentration leads to slight change in the magneto-optical spectra. The effect was more significant in the wavelength range of visible light, and larger for $NiFe_2O_4$ particles than for Fe_3O_4 particles. The external magnetic field influences on the magnetic order and arranges magnetic moments of the nanoparticles by both magnetizing and by rotation of the magnetic moments in the same direction. The ferromagnetic resonance line of $NiFe_2O_4$ nanoparticles is strongly asymmetric, which may be caused by the fact that the powder presents and connects the other type of $Ni_xFe_{2-y}O_4$.

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