ISSN 1027-5495. Functional Materials, 23, No.4 (2016), p. 618-623.
doi:https://doi.org/10.15407/fm23.04.618

Simulation of the electron spin resonance peak shape for magnetic nanopowder formed by particles of different diameters

***T.Kalmykova*[1], *A.Vakula*[1], *S.Nedukh*[1,2], *S.Tarapov*[1,2,3], *A.Belous*[4], *O.Yelenich*[4]**

[1]O.Usikov Institute for Radiophysics and Electronics, National Academy of Sciences of Ukraine, 12 Proskura Str., 61085 Kharkiv, Ukraine
[2]V.Karazin Kharkiv National University, 4 Svobody Sq., 61022 Kharkiv, Ukraine
[3]Kharkiv National University of Radio Electronics, 14 Nauky Ave., 61166 Kharkiv, Ukraine
[4]Institute of General and Inorganic Chemistry, 32/34 Palladina Blvd., Kyiv 03142, Ukraine

Received August 28, 2016

Results of simulation of shape of the electron spin resonance absorption peak for magnetic nanopowder are presented. The influence of magnetic particle diameter on the shape and on width of the resonance peak is shown. The role of internal magnetic anisotropy field is under discussion. The simulation results show a good agreement with the experimental data of the electron spin resonance absorption in a) Fe_3O_4_Triton, b) Fe_3O_4_Crio, nanopowder and the data of its X-ray analysis.
Keywords: electron spin resonance, magnetic nanopowder, magnetic anisotropy.

Представлены результаты моделирования формы пика поглощения электронного спинового резонанса для магнитного нанопорошка. Показано влияние диаметра магнитных частиц на форму и на ширину резонансного пика. Роль анизотропии внутреннего магнитного поля находится на стадии обсуждения. Результаты моделирования и данные рентгеновского анализа показывают хорошее согласование с экспериментальными данными резонансного поглощения спина электрона в а) Fe_3O_4_Triton, б) Fe_3O_4_Crio, нанопорошках.

Моделювання форми піку електронного спінового резонансу для магнітного нанопорошку, утвореного частками різного діаметра. *Т.В.Калмикова, А.С.Вакула, С.В.Недух, С.І.Тарапов, А.Г.Білоус, О.Еленіч.*

Представлено результати моделювання форми піку поглинання електронного спінового резонансу для магнітного нанопорошку. Показано вплив діаметра магнітних часток на форму і на ширину резонансного піку. Роль анізотропії внутрішнього магнітного поля знаходиться на стадії обговорення. Результати моделювання та дані рентгенівського аналізу показують гарне узгодження з експериментальними даними резонансного поглинання спінів електрона в а) Fe_3O_4_Triton, б) Fe_3O_4_Crio, нанопорошках.

1. Introduction

Nanopowdered magnetic materials are of strong interest for modern physics. This is caused by their prospective applications at the novel technologies for storage of information, in development of novel absorbing microwave materials, for medicine and biology [1, 2]. In particular, the interest is caused by the possibility of these materials usage for treatment of oncological diseases [3, 4].

Necessary to note, that application of magnetic nanopowders suggests their dissolving in various dielectric matrixes, namely in liquids [1–4]. It is known that physical properties of the magnetic material (for example, Fe_2O_3, Fe_3O_4) depends strongly whether the magnet is in the crystalline\polysrystalline phase or it is milled into the nanodisperse powder [5]. It is shown also that magnetic properties of the nanopowder depend on material and phase condition of the dielectric matrix which surrounds it [6].

Method of Electron Spin Resonance (ESR) is one of the most sensitive and informative methods for research of fundamental properties of magnetic nanostructures. However, interpretation of experimental results of the ESR measurements is ambiguity without correct counting of essential features of particles, which form the nanopowder (their size, shape, environment/matrix).

In the given work an attempt to explain the dependence of magnetic properties of magnetic nanopowder on particles size and shape is presented. The explanation is carried out using the analysis of numerical simulation of the ESR-peak shape and comparison with the experiment.

There is work [7] which investigated the magnetic properties of maghemite (c–Fe_2O_3) nanoparticles formed within size-constraining Listeria innocua (LDps) — (DNA-binding protein from starved cells) protein cages that have an inner diameter of 5 nm. It is shown that the spectrum of resonance depends on superparamagnetic fluctuations and inhomogeneous broadening. It is also shown that with increasing temperature the line width is narrowed. The paper compares two models, which simulate the temperature dependence of the line shape.

In the first model it is used the truncated lognormal distribution of particle size or bi-model distribution, and then the form of the Landau-Lifshitz line to describe the resonance of the nanoparticles. An essential feature of this model is that the small particles have the narrow line width and a constant region $g \approx 2$ resonance, while larger particles have the broad resonance lines and undergo a shift in the resonance region.

The second model assumes the uniform particles with diameter of about 4 nm, and random distribution of the uniaxial anisotropy. This model uses the more accurate calculation of the line width associated with super paramagnetism fluctuation and the random distribution of anisotropy. The both models can explain many features of the observed spectra, but each has its drawbacks. The first model leads to increase in the magnetic moment. In the second model, there is significant discrepancy between the experimental low-temperature spectra calculated.

In [8] it is proposed a phenomenological model describing the ferromagnetic resonance phenomenon in granular magnetic nanostructure $(SiO_2)_{100-x}Co_x/GaAs$. It is shown that granular magnetic clusters can be formed in the nanostructure, the shape of the clusters depends on concentration of the magnetic material. However, the influence of the particle diameter on shape of the magnetic resonance line is not studied. Thus, in simulation of the electron spin resonance processes remain a number of unresolved problems. This work is a continuation of the research initiated in [8].

2. Experimental

Synthesis of Fe_3O_4 nanoparticles by microemulsion method was performed using Triton X-100 as surfactant, NH_4OH, cyclohexane, butyl alcohol and distilled water as a precipitator, oil phase, co-surfactant and dispersing medium, respectively and Fe_3O_4 nanoparticles synthesized by cryochemical. As the starting reagents $FeSO_4$ and $FeCl_3$ with concentration 1.78 mol/l and 0.96 mol/l, respectively, were used [9].

Results of X-ray diffraction analysis, which show the grain size distribution (in the range of 5–25 nm) are shown in (Fig. 1a,b) for these samples. As well the electron microscope imaging is given in (Fig. 1c,d).

The experiment was carried out at room temperature of T = 300 K, using VNA-spectrometer of Electron Spin Resonance [10]. The spectrometer designed on the base of Vector Network Analyzer Agilent PNA-L N5230A. For studies at T = 300 K we used the experimental module that consists of a set of bulk and waveguide resonator experimental cells [10]. During the experiment the resonator was placed between the poles of electromagnet. The mutually perpendicular orientation of the external magnetic field and magnetic component of the alternating field was provided.

The studies recorded spectra passing the microwave wavelength in the range of 10–40 GHz by the sample. The module works in conjunction with Network Analyzer NA 5230A. There by providing the possibility of different operating modes of the magnetic resonance spectrometer, namely as

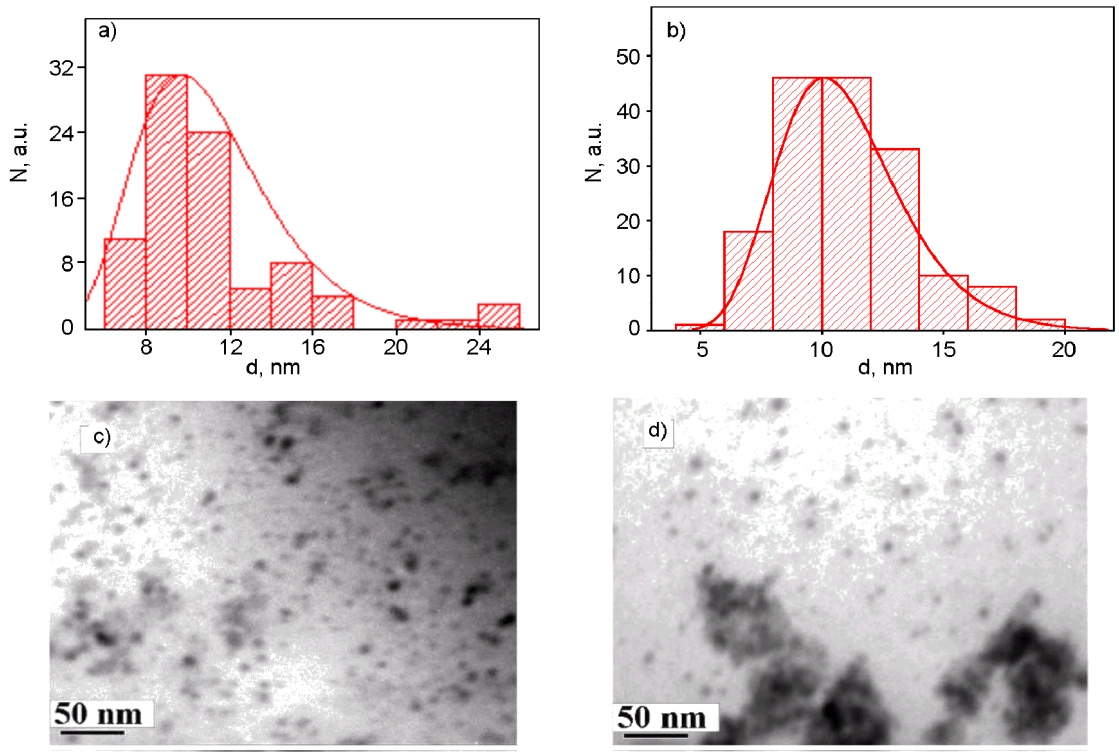

Fig. 1. Distribution of particles by diameter a) Fe_3O_4_Triton, b) Fe_3O_4_Crio, an electron microscope imaging, c) Fe_3O_4_Triton, d) Fe_3O_4_Crio.

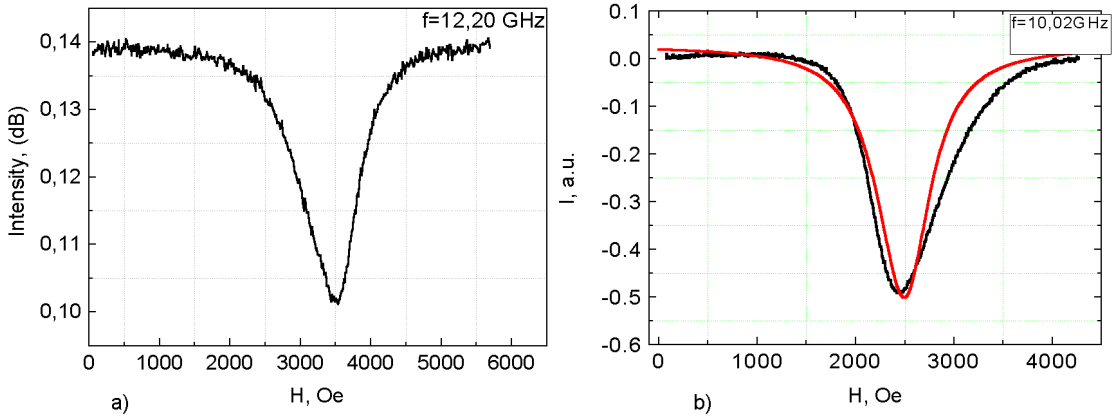

Fig. 2. Experimental spectrum of ESR-peak for nanopowder a) Fe_3O_4_Triton, b) Fe_3O_4_Crio.

scanning the operating frequency at a constant magnetic field and magnetic field scanning (traditional method) while keeping the operating frequency of up to 1–10 Hz.

In the course of the experiment, the ESR peak shape for Fe_3O_4_Triton nanopowder was detected (Fig. 2a) and the ESR peak shape for Fe_3O_4_Crio nanopowder was determined too (Fig. 2b).

3. Results and discussion

As is known, the value of circular resonant frequency ω_{res} for any case of Electron Spin Resonance can be determined by

$$\omega_{res} = \gamma H_{eff}^{res}, \quad (1)$$

where H_{eff}^{res} is the effective resonant magnetic field, γ is the gyromagnetic ratio.

The equation $H_{eff}^{res} = H_{eff}$ depends on the external permanent magnetic field H_0 and on the anisotropy field H_{aniz} as well.

The effective magnetic energy of a single magnetic nanoparticle can be defined as:

$$W_{eff} = W_0 + W_K + W_{dip} + W_s + \ldots, \quad (2)$$

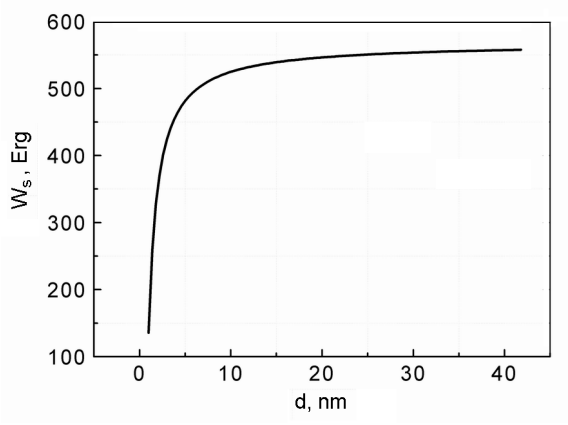

Fig. 3. Dependence of effective energy magnetic field of surface anisotropy for magnetic particle on its diameter.

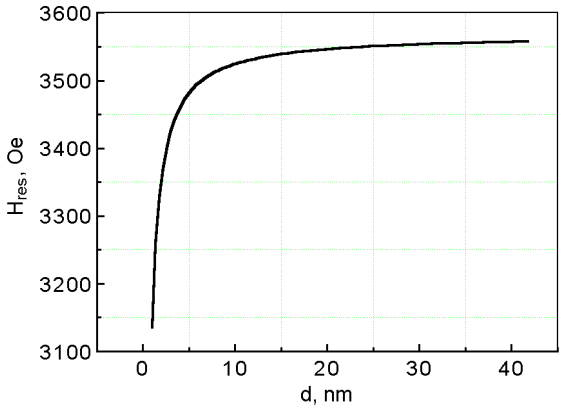

Fig. 4. Dependence of resonance magnetic field on diameter of a single particle at the fixed frequency.

where W_{eff} is the magnetization energy, which defines in the effective magnetic field H_{eff}. It consists of a several components, such as: W_0 — the energy of interaction of spins with the external magnetic field (the Zeeman energy); W_K — the energy of the magnetic crystallographic anisotropy; W_{dip} — the energy of the dipole-dipole interaction; W_s — the surface anisotropy energy.

Since the particles of nanopowder are located in the random order and the crystallographic axes are also randomized, we can assume that the magnetization vector for the particles coincides with direction of the external magnetic field H_0 [10, 11]. Thus, the total anisotropy energy W_K can be considered close to zero.

It is possible to share the contribution of dipole anisotropy on contribution of the shape anisotropy for the single nanoparticle and on contribution of the dipole-dipole interaction between neighbor particles. In the approach of spherically shaped nanoparticles the demagnetization field tends to zero. Features of technology of the sample processing leads to the situation, when field of the dipole-dipole interaction (H_{dip}) is negligible [11] small.

Thus, the expression 1.2 acquires the form:

$$W_{eff} \approx W_0 + W_s, \tag{3}$$

where W_s can be written on the basis of [12] as:

$$W_s = \frac{2K_s}{d}, \tag{4}$$

where K_s is the constant of surface anisotropy, d is the particle diameter.

Thus, the condition of Electronic Spin Resonance for single particle of the nanodisperse powder can be written as:

$$\omega_{res} = \gamma\left(H_0 + \frac{2K_s}{dM_{eff}}\right), \tag{5}$$

where M_{eff} is the effective magnetization.

Considering the size distribution of particles given in Fig. 1 we can calculate the energy (the effective magnetic field of surface anisotropy) for the single particle. Accordingly to [8] let's introduce that sizes of the magnetic particles in the powder are distributed on diameter by the lognormal law:

$$P_i = \frac{L}{\Delta P(d_i)} \cdot \exp\left\{-\frac{\ln(\frac{d_i}{x})^2}{2 \cdot \Delta P^2}\right\}, \tag{6}$$

where L is the normalization constant; x is the predominant grain diameter; d_i is the diameter of i-th particle/pellet; ΔP is the width of lognormal distribution at the half maximum. The result of calculation is given in Fig. 3.

One can see from Fig. 3 that while the diameter (d) of a particle varies from 1 to 20 nm the contribution into the surface anisotropy energy value (the effective magnetic field of surface anisotropy) varies significantly. The contribution of the particles with diameter more than 20 nm absents practically.

In Fig. 4 the calculation of dependence of resonant field of a single particle on its diameter (d) is presented (using the distribution Fig. 1) with the fixed linear frequency f = 12.20 GHz.

In a real situation, the Electron Spin Resonance in the nanopowders immersed into a liquid dielectric matrix represents the superposition of the resonant responses

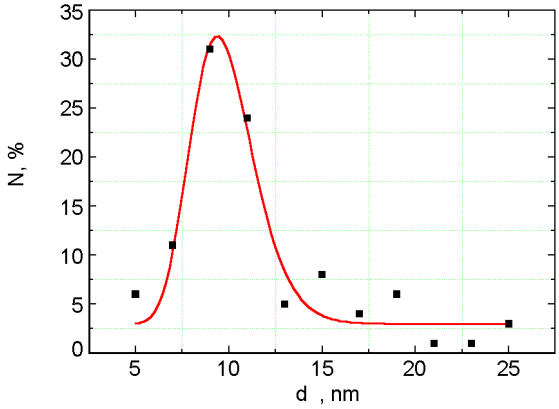

Fig. 5. Lognormal distribution on particle diameter (d): squares note the number of particles (N, %) of a certain diameter. Data received by method of X-ray diffraction, the peak — is the calculated distribution.

contribution into the total effective magnetic field. Moreover the contribution depends on the diameter of the magnetic particle.

Now, by modifying the approach offered in [8], we estimate the shape of the peak of Electron Spin Resonance absorption, taking into account the dispersion of particles by size.

The comparison of the approximated distribution of particles by size and measured by method of X-ray diffraction is presented in Fig. 5. Easy to show that the distribution of particle on the diameter obeys to the lognormal law.

Let's suppose the ESR-response for a single particle is represented by the non-uniformly broadened Lorentz peak.

(7)

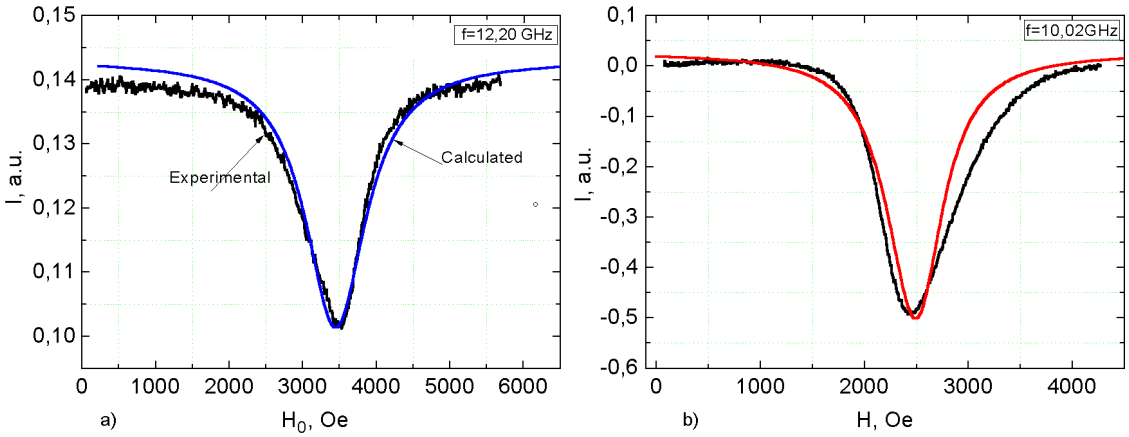

Fig. 6. Experimental and simulated ESR-peaks for nanopowder a) Fe_3O_4_Triton, b) Fe_3O_4_Crio.

from each particle. As it was already stated above, the case of strongly diluted suspensions is considered by us. In this case we neglect by the dipole-dipole interaction between particles that, as a rule, leads to broadening of the ESR-peak [14].

It is known that the broadening of the electron magnetic resonance absorption peak can be occurred besides dipole interaction due to distribution of the magnetic nanoparticles by shape [8].

In the case under analysis we suggest that the shape of particles has a very small deviation from the ideally spherical shape. Thus, we neglect by the dispersion of demagnetizing fields inside each single particle.

It is naturally to assume that in the given case the dispersion of the surface anisotropy field causes the total ESR-peak broadening. As it was shown above, the estimating calculations confirm that the field of surface anisotropy can bring the essential

$$I_i(H) = \frac{1}{1 + \left(\frac{H - H_{(res)i}}{\Delta H_{d_i}} \right)^2},$$

where $H_{(res)i}$ is the resonant magnetic field for i-th particle, ΔH_{di} is the half-width of the ESR-peak for particle, having diameter (d). We assume that the width of the ESR-peak for a single particle is equal to the line width for the bulk sample Fe. Let's suppose that the half line width for the single particle equals to the half line width for the massive specimen.

Thus the total peak of Electron Spin resonance absorption can be approximated [8] by

expression: $Y(H) =$

$$= \sum_{i=1}^{q} \left\{ \frac{1}{1 + \left(\frac{H - H_{(res)_i}}{\Delta H_{d_i}} \right)^2} \cdot \frac{L}{\Delta P(d_i)} \cdot \exp\left\{ -\frac{\ln(\frac{d_i}{x})^2}{2 \cdot \Delta P^2} \right\} \right\}, \quad (8)$$

where the summation is carried out on number (q) of magnetic particles, which size is distributed on the lognormal law (1.6).

The result of calculation using Eq. (1.8) is presented in Fig. 6.

Fig. 6 shows clearly that the experimental data and the result of the simulation of peak shape by expression (1.8) are almost identical. The difference in the peaks shape can be caused most likely by the unaccounted contribution of the crystallographic magnetic anisotropy (which was accepted equals to zero) or by the dipole — dipole interaction.

4. Conclusions

The approach offered allows the interpretation of experimental results within the model of weakly-interacting spherical particles for which the surface magnetic anisotropy is sufficient. Such approach allows to describe the dependence of the shape of Electron Spin Resonance peak on the particles diameter.

References

1. J.L.Dormann, E.Tronc, D.Fiorani, *Adv.Chem. Phys.*, **98**, 283 (1997).
2. J.Kliava, R.Berger, *Recent Res.Devel.Non-Crystalline Solids*, **3**, 41 (2003).
3. J.Gao, B.Xu, *Nano Today*, **4**, 37 (2009).
4. T.-Y.Liu, S.-H.Hu, D.-M.Liu et al., *Nano Today*, **4**, 52 (2009).
5. V.Skumryev, S.Stoyanov, Y.Zhang et al., *Nature*, **423**, 850 (2003).
6. Yuanzhi Chen, *Ceram.Int.*, **27**, 73 (2001).
7. R.J.Usselman, S.E.Russek, M.T.Klem et al., *J.Appl.Phys.*, **112**, 084701 (2012).
8. T.V.Bagmut, *Radio Phys.Electr.*, **13**, 65 (2007).
9. O.V.Yelenich, S.O.Solopan, T.V.Kolodiazhnyi et al., *Sol.St.Phen.*, **230**, 108 (2015).
10. T.V.Kalmykova, S.I.Tarapov, S.V.Nedukh et al., *Functional Materials*, **19**, 486 (2012).
11. L.V.Lutsev, M.N.Kopytin, A.V.Sitnikov et al., *Phys.Sol.Stat.*, **47**, 2169 (2005).
12. E.Limpert, W.A.Stahel, M.Abbt, *BioScience*, **51**, 341 (2001).
13. E.S.Borovic, V.V.Eremenko, A.S.Milner, Lecture on Magnetism, Kharkov University (2005) [in Russian].
14. M.R.Dudek, N.Guskos, M.Kosmider, in: Smart Nanoparticles Technology, ed. by A.Hashim, InTech (2012), Wroclaw p.373.