Determination of the Parameters of Composites with Magnetic Particles from the Study of the Spectra of Ferromagnetic Resonance in the Microwave Frequency Range

V. A. Zhuravlev, V. A. Meshcheryakov, and E. P. Lilenko
Tomsk State University, Tomsk 634050, Russian Federation

Abstract— We calculated the components of the magnetic susceptibility tensor of the composite material consisting of uniaxial magnetic particles in this paper. A method for determining of the anisotropy fields on the basis of analyzing the curves of ferromagnetic resonance in the microwave frequency range is proposed. The results of the study of the magnetic anisotropy obtained by different methods hexaferrite powder samples composition $BaFe_{12}O_{19}$ are analyzed.

1. INTRODUCTION

Active exploration of the microwave frequency range sharpened the need for magnetic materials absorbing electromagnetic radiation. Such materials are required to reduce harmful influence on biological objects, to provide electromagnetic compatibility of units and blocks of high-frequency devices, to build anechoic chambers and to protect information. Composite radar absorbing coating (RAC) which consists of a matrix of high-molecular polymer compounds and filler particles of ferromagnetic or ferrimagnetic materials are widely used. Such materials are most effectively used as electromagnetic waves absorbers located on the metal surfaces [1]. The most promising materials for microwave and submillimeter ranges are ferrites with a hexagonal crystal structure (hexaferrites). This is due to the large values of the anisotropy fields (H_{ai}) and saturation magnetization (M_S) of these materials [2]. It is necessary to know the material parameters (magnetocrystalline anisotropy fields, the gyromagnetic ratio (γ) and saturation magnetization) of the filler particles of the composite material for targeted development and production of RAC in a given frequency range and level of reflectance in the operating band.

The study of the spectra of ferromagnetic resonance (FMR) in the microwave frequency range is one of the few methods to determine the required material parameters such inhomogeneous and macroscopically isotropic materials, including materials with nanosized and nanostructured particles [3, 4]. The development and testing based on the study of FMR methods of determining the characteristics of the anisotropic powder and composite materials is the aim of this work.

To do this, in Section 2 we calculate the permeability tensor of the polycrystalline, powder or composite materials containing randomly oriented particles of uniaxial hexaferrites. In Section 3 we propose based on the analysis of FMR spectra in the microwave frequency range two-stage method of determining the anisotropic characteristics of such composite materials. In the first stage the frequency dependences of the maxima and the derivatives of the resonance curves are analyzed. It gives us the estimation for the gyromagnetic ratio γ and anisotropy fields H_{ai}. In the second stage by a detailed comparison the shape of experimental and theoretical resonance curves we obtain more accurate values of the anisotropy field. In Section 4 we present the results of applying this method to determine the anisotropic characteristics of polycrystalline samples of hexaferrites and composite materials containing nanosized ferrimagnetic particles.

2. MAGNETIC SUSCEPTIBILITY TENSOR OF THE COMPOSITE MATERIAL CONTAINING RANDOMLY ORIENTED PARTICLES OF UNIAXIAL HEXAFERRITES

As a rule, the anisotropy field of hexaferrites in the basal plane (H_Φ) is significantly smaller than the anisotropy field with respect to the hexagonal axis c (H_Θ). Therefore, for the analysis of the FMR in such composite materials we may consider only uniaxial anisotropy field H_Θ and anisotropy field H_Φ can be ignored. The magnetic susceptibility tensor of anisotropic magnets in general form was obtained in [5]. For polycrystalline and composite materials with uniaxial anisotropy in the independent grains approximation its components can be written as:

$$\chi = 0.5c_M\langle(\chi_{11} + \chi_{22})\rangle_\Theta, \quad \chi_\| = c_M\langle\chi_{33}\rangle_\Theta, \quad \pm i\chi_a = c_M\langle\chi_{12(21)}\rangle_\Theta. \tag{1}$$

Here c_M is the magnetic particles concentration in the composite, $\langle \ldots \rangle_\Theta$ denotes averaging over the polar angle of the tensor components of monocrystalline grain $\overleftrightarrow{\chi}$:

$$\begin{aligned}
&\chi_{11} = (\gamma M_S/Zn)\,[\Omega_1 + i\omega\alpha], \quad \chi_{22} = (\gamma M_S/Zn)\cos^2(\Theta - \vartheta_0)[\Omega_2 + i\omega\alpha],\\
&\chi_{33} = (\gamma M_S/Zn)\sin^2(\Theta - \vartheta_0)[\Omega_2 + i\omega\alpha], \quad \chi_{12(21)} = \pm i\omega\,(\gamma M_S/Zn)\cos(\Theta - \vartheta_0),\\
&\Omega_1 = \gamma\,[H_0\cos(\Theta - \vartheta_0) + H'_{a1}\cos(2\vartheta_0), \quad \Omega_2 = \gamma H_0 \sin\Theta/\sin\vartheta_0,\\
&Zn = \omega_0^2 - \left(1+\alpha^2\right)\omega^2 + i2\omega\omega_r, \quad \omega_0^2 = \Omega_1\Omega_2, \quad \omega_r = (1/2)\alpha\,(\Omega_1 + \Omega_2)\,.
\end{aligned} \tag{2}$$

Here: α — damping constant in the Landau-Lifshitz equation, $H'_{a1} = 2k_1/M_S - 4\pi M_S(N_\| - N_\perp)$ — magnetocrystalline anisotropy field with the additives on the shape anisotropy, $N_\|$, $N_\perp$ — demagnetization factors of ellipsoidal particles. k_1 — is the first magnetocrystalline anisotropy constant. Equilibrium angle (ϑ_0) of the magnetization vector is found by solving the transcendental equation:

$$H_0\sin(\Theta - \vartheta_0) = (1/2)\sin 2\vartheta_0 H'_{a1} \tag{3}$$

for a given value of the magnetizing field (H_0) and his orientation (Θ).

3. DETERMINATION OF ANISOTROPIC CHARACTERISTICS FROM THE STUDY OF THE FMR SPECTRA IN THE MICROWAVE FREQUENCY RANGE

The FMR curves obtained from the polycrystalline or powdered specimens contain two types of singularities — maximums and kinks. The low-field singularity corresponds to the resonance of crystallites whose magnetization-field direction **is close to the easy magnetization axis** (EMA). The high-field singularity corresponds to the resonance of crystallites whose magnetization-field direction **is close to the hard magnetization axis** (HMA). The resonance field (frequency) values for these directions are determined from the following formula [5]:

$$\omega_\| = \gamma_\| \left[H_{res1} + \frac{\gamma_\perp}{\gamma_\|}H'_{a1}\right], \quad \omega_\perp = \gamma_\perp\left[H_{res2}\left(H_{res2} - H'_{a1}\right)\right]^{1/2}. \tag{4}$$

Here $\omega_\|$, $\gamma_\|$ and $\omega_\perp$, $\gamma_\perp$ are the resonance frequencies and the magnetomechanical ratios for directions along the hexagonal axis and those in the base plane, respectively.

Figure 1 shows the results of comparing of the parameters of the resonance curve of a polycrystalline sample: maxima (M) on the curves of the FMR and maximum on first derivatives of the curves of the FMR (FD) with the calculation of the resonance frequencies of the FMR single crystal (lines) according to (4). It is seen that for polycrystals with the EAM fields FD corresponding maximum of the derivative (inflection points) curves FMR, close to the curves calculated by the Formula (4). For materials with EPM for the low-field feature best match with (4) is obtained for the mean fields corresponding to the maximum of the derivative and the maximum of the curve FMR — $(H_{FD} + H_M)/2$, for the high-field feature with the maximum derivative of the H_M. In this

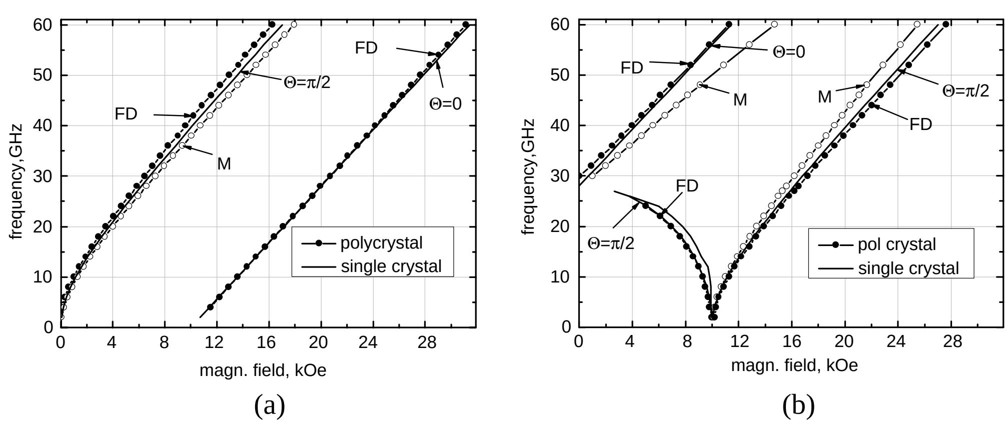

Figure 1: The resonant frequencies of the FMR. (a) For material with anisotropy of easy plane of magnetization (EPM), $H_{a1} = -10\,\text{kOe}$. (b) For material with anisotropy of easy axis of magnetization (EAM), $H_{a1} = 10\,\text{kOe}$. Damping constant in the equation of motion $\alpha = 0.1$. $\gamma_\perp = \gamma_{||} = 2.8\text{GHz/kOe}$.

regard, experimental processing polycrystalline FMR spectra to determine the anisotropic characteristics of materials were carried out in two stages. At the first stage the dependencies of resonance frequencies on the magnetizing field corresponding to the maximum of the derivative or the average value $(H_{FD}+H_M)/2$ are constructed. By treatment of these dependencies by least squares method using the Formula (4) the values $\gamma_{\|}$, $\gamma_{\perp}$ and approximate values of the anisotropy field H'_{a1} are estimated. Further, by detailed comparison of the calculated according to the formulas (1)–(3) and experimental FMR curves the values of anisotropy fields are corrected.

4. STUDY THE MAGNETIC ANISOTROPY OF $BaFe_{12}O_{19}$ HEXAFERRITE POWDER SAMPLES

The results of the study of the phase composition, structural parameters and magnetic properties of nanosized powders of barium hexaferrite M-type composition $BaFe_{12}O_{19}$ (Ba-M) are given in this chapter. Sample No. 1 obtained by sol-gel combustion. Sample No. 2 made of commercially available of permanent magnets brands 19BA260. Magnet was demagnetizing by heating above the Curie temperature, holding at 600°C for 2 h and cooling off oven. Then it was milled in a planetary ball mill. For the experiments we used the fraction of agglomerates of particles with a size less than 60 microns.

According to Table 1, the contents of the main phase of Ba-M in both samples is greater than 97% and an additional phase is a magnetite. Samples has similar lattice constant a and the same values of the lattice constant along the hexagonal axis c. These results are correspond to well-known from the literature for hexaferrite Ba-M. Based on the analysis of the physical broadening of the diffraction lines the sizes of coherent scattering domains (CSD) and values of internal elastic microstrains, proportional to the relative change in interplanar distances $(\Delta d/d)$ was evaluated. These options for both samples are also close to each other.

Processing of the experimental FMR spectra of samples No. 1 and No. 2, taken in the frequency range 37–53 GHz, performed as described above. Figure 2 shows the calculated in the independent grains approximation imaginary parts of the diagonal components of the permeability tensor (line) and experimental FMR curves (points) of samples No. 1 (Figure 4(a)) and No. 2 (Figure 4(b)) for the two frequencies. The tensor components were calculated for the saturation magnetization value equals 366 Gs (No. 1) and 385 (No. 2). The experimental curves were normalized to the theoretical. The measurement frequencies are given in the figure caption.

The maximum on the FMR lines shifts towards smaller fields with a decrease in the frequency. The growth in losses at zero field with decreasing frequency was due to the approach of the frequency

Table 1: The phase composition of the investigated materials.

Sample	The phase composition of the samples, vol. %		Lattice constants, Ǎ		CSD, nm	$\Delta d/d*10^3$
	$BaFe_{12}O_{19}$	Fe_3O_4	a	c		
No. 1	98.6	1.4	5.9139	23.3130	87	1.3
No. 2	97.4	2.6	5.9089	23.3130	80	1.1

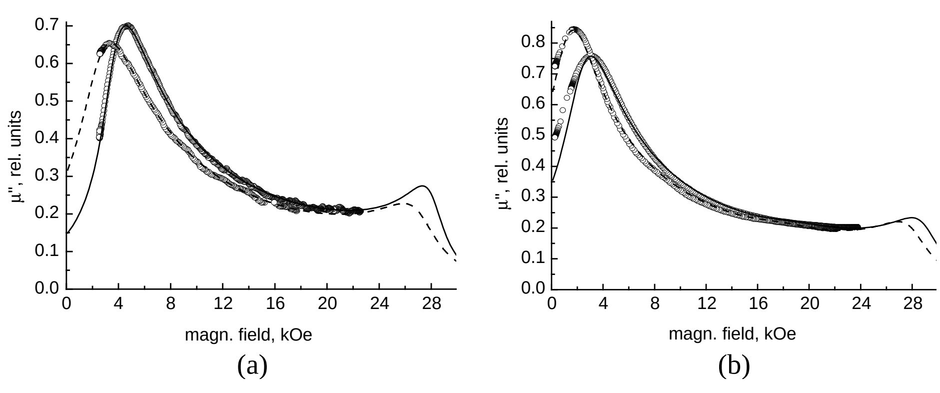

Figure 2: FMR curves of (a) sample No. 1 and (b) sample No. 2. Solid lines — the frequency of 53 GHz, dashed — 50 GHz.

Table 2: Magnetic parameters measured by FMR methods.

Sample	$\gamma/2\pi$, GHz/kOe	H'_{a1}, kOe	α
No. 1 frequency of 50 GHz	2.80 ± 0.02	15.4 ± 0.1	0.11 ± 0.01
No. 1 frequency of 53 GHz	2.80 ± 0.02	15.4 ± 0.1	0.07 ± 0.01
No. 2 frequency of 50 GHz	2.80 ± 0.02	16.7 ± 0.1	0.1 ± 0.01
No. 2 frequency of 53 GHz	2.80 ± 0.02	16.7 ± 0.1	0.09 ± 0.01

of microwave magnetic field to the frequency of the natural ferromagnetic resonance (NFMR), defined by the formula:

$$\omega_{\text{NFMR}} = \gamma_{\perp} H'_{a1}. \tag{5}$$

The values of the magnetomechanical ratios, the anisotropy fields and the damping constants in the Landau-Lifshitz-Gilbert equation presented in Table 2. According to Table 2, the measured values of the magnetomechanical ratios synthesized by different methods samples are the same as the gyromagnetic ratio for the spin of a free electron within experimental error. The effective anisotropy field sample No. 2 close to the literature data for hexaferrite Ba-M [2], while for the sample No. 1 it is noticeably smaller. The impact of contribution of the shape anisotropy of the particle is possible reason for this.

Sample No. 2 is composed of particles with sizes less than 60 microns. Particles of this sample consists of agglomerates of nanoparticles with CSD ≈ 80 nm. We can assume that the shape of the particles sample No. 2 are nearly spherical and the demagnetizing field do not contribute to the total magnetic anisotropy.

Then the difference between the anisotropy fields of samples No. 1 and No. 2 can be attributed to the addition of the shape anisotropy of grain: $4\pi M_S(N_{\perp} - N_{\parallel}) \approx -1.3$ kOe. Hence it was estimated for the demagnetizing factor of the particle sample No. 1: $N_{\perp} \approx 0.24$, $N_{\parallel} \approx 0.52$. They correspond to an oblate spheroid with an axis ratio ≈ 2. This is a realistic estimation of the shape anisotropy of single-domain nanoparticles with hexagonal crystal structure [2].

5. CONCLUSION

In the paper we propose a method for processing FMR spectra in inhomogeneous materials with uniaxial magnetic anisotropy, such as polycrystalline or powder ferrimagnetics and composites based on them. The technique makes it possible to determine from the experiments the important anisotropic characteristics uniaxial magnetic particles. A comparative analysis of the properties of hexaferrite powders $BaFe_{12}O_{19}$, obtained by the sol-gel combustion and grinding commercially available magnets 19BA260 brand was performed.

ACKNOWLEDGMENT

This Research is supported by Tomsk State University Competitiveness Improvement Program.

REFERENCES

1. Bystrov, R. P., V. G. Dmitriev, Y. A. Zemskii, Y. M. Perunov, and V. A. Cherepenin, "Special features of the development of the radio-technical systems of the radio-electronic struggle," *Uspekhi Sovremennoi Radioelektroniki (Achievements of Modern Radioelectronics)*, No. 8, 3–28, 2012.
2. Pullar, R. S., "Hexagonal ferrites: A review of the synthesis, properties and applications of hexaferrite ceramics," *Progress in Material Science*, Vol. 57, No. 7, 1191–1334, 2012.
3. Zhuravlev, V. A. and E. P. Naiden, "Dependence of the structural parameters and magnetic properties of nanoscale powders of hexaferrite Zn_2Y on the mechanical activation regimes," *Physics of the Solid State*, Vol. 51, No. 2, 327–333, 2009.
4. Naiden, E. P., V. A. Zhuravlev, V. I. Itin, R. V. Minin, V. I. Suslyaev, and O. A. Dotsenko, "Structure and static and dynamic magnetic properties of $Sr(Co_xTi_x)Fe_{12-2x}O_{19}$ hexaferrites produced by self-propagating high-temperature synthesis," *Russian Physics Journal*, Vol. 55, No. 8, 869–876, 2013.
5. Zhuravlev, V. A. and V. A. Meshcheryakov, "Magnetic susceptibility tensor of anisotropic ferromagnetic magnetized media," *Russian Physics Journal*, Vol. 56, No. 12, 1387–1397, 2014.