ISSN 1063-7834, Physics of the Solid State, 2015, Vol. 57, No. 10, pp. 2011–2015. © Pleiades Publishing, Ltd., 2015.
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Application of Tsallis Functions for Analysis of Line Shapes in Electron Magnetic Resonance Spectra of Magnetic Nanoparticles

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Received April 14, 2015

Abstract—An effective electron magnetic resonance study of nanoparticles requires, in addition to an adequate theory (which is absent nowadays), standard spectral characteristics making it possible to compare the spectra. For characterizing the electron magnetic resonance spectra of magnetic nanoparticles, it has been proposed to use the decomposition of the spectra using the parameters of Tsallis distributions (lines with smoothly varying shapes). This method has been tested on a two-component spectrum of colloidal magnetite nanoparticles and on poorly resolved broad spectra of iron-containing nanoparticles stabilized on microgranules.

DOI: 10.1134/S1063783415100121

1. INTRODUCTION

At present, the interpretation of electron magnetic resonance (EMR) spectra of magnetic nanoparticles is a difficult problem [1]. The reasons are the incompleteness of the EMR theory of such objects and a significant inhomogeneity of the internal structure of nanoparticles and systems on their basis. As a result, in many publications, the EMR spectra of magnetic nanoparticles are described qualitatively with the simplest parameters: the effective resonance field (or the effective *g*-factor) and the line width determined by the peak-to-peak method. However, for comparing the results of the analysis of nanoparticles with close chemical compositions and sizes but obtained in different laboratories or by different methods in the same laboratory, a more detailed quantitative description of the EMR line shape is necessary.

The existing theoretical approaches [1–3] to the analysis of the EMR spectra of magnetic nanoparticles are based on the adaptation of the classical theory of ferromagnetic resonance of single-domain particles with a collinear internal magnetic structure [4] for the case of strong thermal fluctuations of the direction of the total magnetic moment, which are typical of superparamagnetic nanoparticles above the blocking temperature [5]. In the approach described in [1], the inclusion of superparamagnetic fluctuations in the analysis leads to the necessity of solving the Fokker–Planck equation. In [2, 3], the authors solved the Landau–Lifschitz–Gilbert equation under different assumptions on the influence of superparamagnetic fluctuations on the magnetic parameters of particles. In [6], the effects of quantization of the magnetic moment of a nanoparticle additionally were taken into account.

However, the methods used for the calculation of EMR spectra of magnetic nanoparticles, described in literature [1–3, 6], have not been widely accepted yet for a number of reasons. In particular, their implementation requires to choose a theoretical model of calculation, to correctly specify the ranges of model parameters, which are not always known from the experiment, to solve a system of differential equations, and to perform a procedure of multiparametric fitting of the experimental and theoretical spectra. Solving this problem is often complicated by an extremely large width and complex shape of the EMR spectra of magnetic nanoparticles, which additionally complicates the unique choice of parameters of the theoretical model.

In this work, a relatively simple method has been proposed for the quantitative line shape analysis of EMR spectra of magnetic nanoparticles. In particular, this method employs formulas—well-known in EMR spectroscopy—for calculating the spectra of polycrystals with anisotropic magnetic centers, which are the superposition of the contributions from individual differently oriented crystallites. However, in contrast to the standard approach, the line shape of an individual contribution is specified by means of a Tsallis function [7, 8]. The application of the Tsallis functions enables one—in addition to the anisotropy of the resonance field and EMR line width—to use the possible line shape anisotropy of an individual component of an inhomogeneously broadened EMR spectrum. The proposed method can help many researchers to obtain quantitative line-shape characteristics of complex EMR spectra of magnetic nanoparticles, convenient for practical use.

2. “POLYCRYSTALLINE” FORM OF THE EMR LINE OF SUPERPARAMAGNETIC NANOPARTICLES

The EMR spectra of paramagnetic centers characterized by an anisotropic g-factor (g-tensor) have a typical “polycrystalline” form [9]. In a system of randomly oriented ellipsoidal superparamagnetic nanoparticles, each particle is characterized by the anisotropy of the resonance field H_R, which can be converted into the g-factor by the formula

$$g = 2.0023 H_e / H_R, \tag{1}$$

where H_e is the resonance field for a free electron. In the simplest case (without regard for superparamagnetic fluctuations), the g-tensor of a particle can be obtained, e.g., from Kittel’s formula [4]. Of course, superparamagnetic fluctuations can change the parameters of the g-tensor of an individual particle but the resulting EMR spectrum of the system of randomly oriented nanoparticles should retain the “polycrystalline” form. In this case, for simulating the spectrum of a system of randomly oriented superparamagnetic nanoparticles, one may try to apply formulas that are traditionally used for paramagnetic anisotropic centers. The formulas for calculating the EMR spectrum can be written in the form [9]

$$I(H) = \iint g_p S(H - H_R) \sin\theta d\theta (d\varphi), \tag{2}$$

where $S(H - H_R)$ is the resonance line (the derivative of the absorption) for an individual nanoparticle and g_p is a factor characterizing the anisotropy of the transition probability.

Having chosen the Cartesian coordinates with the axes directed along the principal axes of the ellipsoid of a particle, one can write the formula for the g-factor of the particles as [9]

$$g^2 = g_x^2 l_x^2 + g_y^2 l_y^2 + g_z^2 l_z^2, \tag{3}$$

where l_i ($i = x, y, z$) are the direction cosines of the external magnetic field H with respect to the axes of the Cartesian coordinates.

The parameter g_p for the transition probability can be written in the form [9, 10]

$$g_p = g_1^2 / g^3, \tag{4}$$

$$g_1^2 = (g_x g_y (1 - l_z^2) + g_x g_z (1 - l_y^2) + g_y g_z (1 - l_x^2)) / 2g^2. \tag{5}$$

As was shown in [9], the quantity g_p in (4) can be replaced within ~1% with

$$\begin{aligned} g_p = {} & (2/3)\{(g_x^2 + g_y^2 + g_z^2)/3\}^{1/2} \\ & + (1/9)(g_x + g_y + g_z). \end{aligned} \tag{6}$$

Considering the magnetic moment of a nanoparticle as a “microspin,” i.e., assuming a collinear magnetic structure inside the particle, one may expect that formulas (3) and (6), which were obtained for paramagnetic centers, must hold for nanoparticles as well.

In addition to the anisotropy of the g-factor, the analysis of polycrystalline EMR spectra sometimes takes into account the anisotropy of the line width [11]:

$$\Delta H^2 = \Delta H_x^2 l_x^2 + \Delta H_y^2 l_y^2 + \Delta H_z^2 l_z^2. \tag{7}$$

The similarity of formulas (3) and (7) suggests that the principal axes of the tensors describing the anisotropy of the g-factor and the line widths coincide. Moreover, the dependence (7) itself is caused by inhomogeneous broadening [11].

The shape of an individual line $S(H - H_R)$ in (2) is usually chosen Gaussian or Lorentzian. In [7], for the first time, it was proposed to use the Tsallis distribution [12] for the computer analysis of EMR spectra. The Tsallis distribution is defined by the relationship [8]

$$\begin{aligned} & Y(H - H_R) \\ & = Y_{\max}\{1 + (2^\alpha - 1)[(H - H_R)/\Gamma]^2\}^{-1/\alpha} \end{aligned} \tag{8}$$

for the absorption signal and

$$\begin{aligned} Y_1(H - H_R) = {} & -2Y_{\max}\{(2^\alpha - 1)(H - H_R)/(\alpha\Gamma^2)\} \\ & \times \{1 + (2^\alpha - 1)[(H - H_R)/\Gamma]^2\}^{-(1+\alpha)/\alpha} \end{aligned} \tag{9}$$

for the derivative of the magnetic field absorption signal $Y_1(H - H_R) = dY(H - H_R)/dH$. Standard EMR spectrometers detect $Y_1(H - H_R)$.

In formulas (8) and (9), Γ is the half-width of line (8) at half-maximum, $Y_{\max} = Y(H_R)$ is a normalization constant, and $\alpha \equiv q - 1$, where q is the parameter of the Tsallis distribution. It should be noted that $q \in (1; +\infty)$; as $q \longrightarrow 1$, function (8) is transformed to the Gaussian distribution and, at $q = 2$, to the Lorentzian distribution. Thus, the Tsallis function enables one to simulate a smooth variation in the shape of a resonance line from Gaussian ($q \longrightarrow 1$) to Lorentzian ($q = 2$) and, further on, to super-Lorentzian ($q > 2$). The

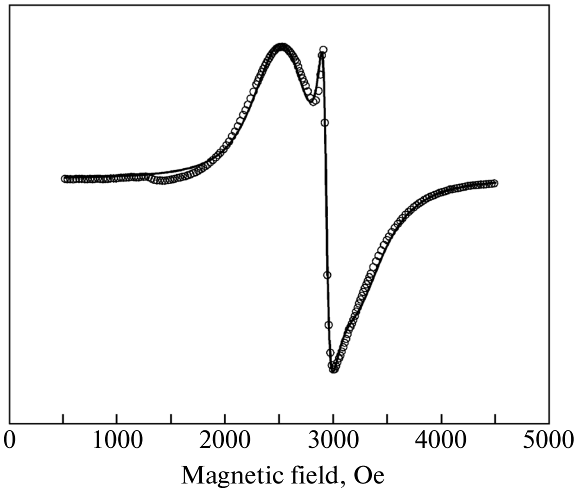

Fig. 1. EMR spectrum of colloidal magnetite nanoparticles. Points are the experimental data, and the solid line shows the sum of two Tsallis distributions. The parameters of the Tsallis distributions are presented in the text. The spectra were recorded at room temperature on a Varian E-4 spectrometer.

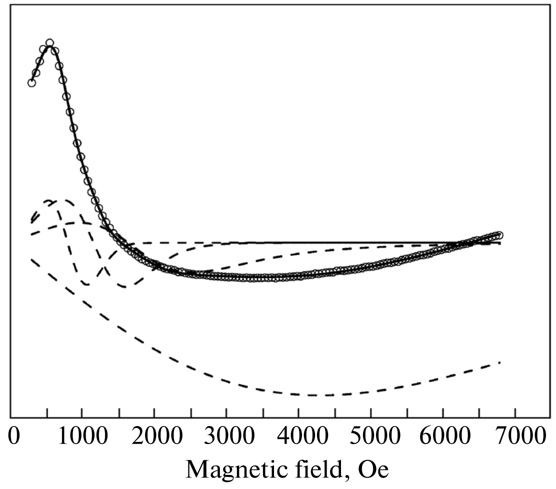

Fig. 2. EMR spectrum (at $T = 295$ K) of α-Fe nanoparticles on the surface of silicon oxide microgranules. Points are the experimental data, and the solid line shows the sum of four Tsallis distributions (represented by dashed lines). The parameters of the Tsallis distributions are presented in the text.

anisotropy of the shape of a resonance line can be simulated, e.g., by the formula similar to expression (7):

$$q^2 = q_x^2 l_x^2 + q_y^2 l_y^2 + q_z^2 l_z^2. \qquad (10)$$

Thus, the fitting of an experimental singlet by formula (2), which employs $S(H - H_R) = Y_1(H - H_R)$, involves the variation of ten parameters: $\{g_x, g_y, g_z, \Gamma_x, \Gamma_y, \Gamma_z, q_x, q_y, q_z, Y_{\max}\}$. The anisotropy of Γ may be specified by a formula similar to (3) and (7):

$$\Gamma^2 = \Gamma_x^2 l_x^2 + \Gamma_y^2 l_y^2 + \Gamma_z^2 l_z^2. \qquad (11)$$

If the spectrum has several resolved lines, the number of parameters increases proportionally to the number of lines.

Figure 1 shows the results of the fitting of the EMR spectrum of colloidal magnetite (Fe_3O_4) nanoparticles, used for preparation of magnetic microcapsules, by the sum of two Tsallis distributions. The mean nanoparticle size is ~10 nm, but many of them are united into loose agglomerates [13]. The spectrum has a two-pattern form often occurring in the analysis of iron-containing nanoparticles [14–16].

The sum of two Tsallis distributions provides a good approximation of the experimental spectrum. The parameters of the Tsallis distributions are as follows: $g_x = 2.04$, $g_y = 2.26$, $g_z = 1.83$, $\Gamma_x = 540$ Oe, $\Gamma_y = 235$ Oe, $\Gamma_z = 275$ Oe, $q_x = 1.90$, $q_y = 1.00$, and $q_z = 1.77$ (the broad component); $g_x = 2.00$, $g_y = 2.00$, $g_z = 1.96$, $\Gamma_x = 70$ Oe, $\Gamma_y = 55$ Oe, $\Gamma_z = 135$ Oe, $q_x = 2.33$, $q_y = 2.43$, and $q_z = 1.34$ (the narrow component). The single-valued convergence of the fitting procedure was tested by specifying different initial values of the parameters. The difference between the experimental and calculated spectra was minimized by a computer algorithm used in [17, 18].

The narrow central line in the two-component spectrum of iron-containing magnetic nanoparticles may be assigned to their "fine" fraction in the colloidal system, because the smaller is the particle, the stronger is the effect of the superparamagnetic fluctuations on it [1–3, 6, 19, 20]. The results of the fitting do not contradict the following interpretation: the g-tensor of the narrow signal is practically isotropic, and the magnitudes of its components are ~2.0; the values of the parameters $q > 2$ may indicate the tailing of the resonance line, enhanced with a reduction in the nanoparticle size [19].

It should be noted that the attempts of fitting the considered experimental EMR spectrum with a function $S(H - H_R)$ of a constant form (Gaussian or Lorentzian) gave a significantly worse result than that presented in Fig. 1.

3. APPLICATION OF TSALLIS FUNCTIONS FOR SIMULATION OF WIDE ASYMMETRIC EMR SPECTRA

The EMR spectra of certain types of magnetic nanoparticles can be very broad or asymmetric. For example, Fig. 2 shows the EMR spectrum of α-Fe nanoparticles on the surface of SiO_2 microgranules [21]. In this case, it is inadvisable to simulate spectra of the "polycrystalline" type. The form of such complicated spectra can be quantitatively described by the decomposition of them into a sum of Tsallis distributions. Due to the flexible form of the Tsallis distributions, such decomposition employs a small number of

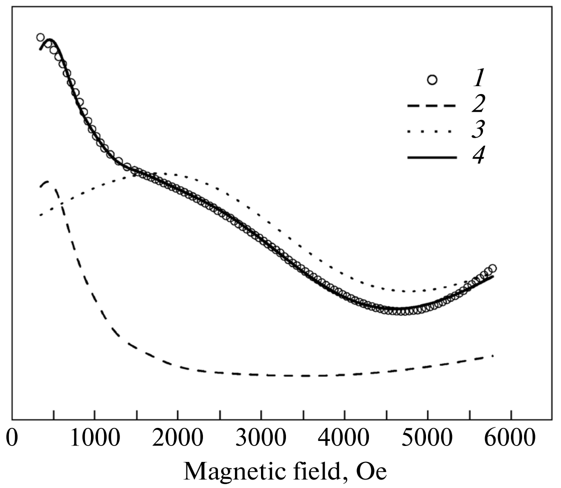

Fig. 3. EMR spectrum (at $T = 295$ K) of iron-containing nanoparticles on the surface of diamond microgranules: (*1*) experimental data, (*2*) "standard" spectrum of α-Fe (see the text), (*3*) the Tsallis distribution corresponding to the γ-Fe_2O_3 phase, and (*4*) the sum of the "standard" spectrum and the Tsallis distribution.

terms as compared to the decomposition into, e.g., the Gaussian distributions. For example, as is evident from Fig. 2, the form of the EMR spectrum of α-Fe nanoparticles can be quantitatively specified by means of only four Tsallis distributions of the form (9) with the following parameters (in the ascending order of H_R): $H_{R1} = 735$ Oe, $\Gamma_1 = 265$ Oe, $q_1 = 1.0$, and $Y_{\max 1} = 2.7$; $H_{R2} = 975$ Oe, $\Gamma_2 = 6120$ Oe, $q_2 = 1.7$, $Y_{\max 2} = 131.3$; $H_{R3} = 1085$ Oe, $\Gamma_3 = 440$ Oe, $q_3 = 1.4$, and $Y_{\max 3} = 5.3$; $H_{R4} = 1580$ Oe, $\Gamma_4 = 1550$ Oe, $q_4 = 2.9$, and $Y_{\max 4} = 12.5$.

The obtained "standard" spectrum of nanoparticles, which dominantly contain α-Fe [21], can be used for the quantitative analysis of the spectrum of iron-based nanoparticles containing, apart from α-Fe, other (as a rule, oxide) phases. For example, Fig. 3 shows the EMR spectrum of iron-containing nanoparticles stabilized on the surface of diamond microgranules [22]. The data of structural methods [22] indicate that such nanoparticles have two phases: α-Fe and γ-Fe_2O_3 (maghemite). The low-field part of the EMR spectrum in Fig. 3 indicates the presence of α-Fe. In order to separate in the EMR spectrum the components corresponding to the α-Fe and γ-Fe_2O_3 phases, it can be decomposed into the "standard" spectrum of α-Fe (Fig. 2) and an additional Tsallis distribution. The result of the decomposition is shown in Fig. 3. The additional Tsallis distribution proved to be close to a Gaussian distribution with the parameters $H_R = 3230$ Oe, $\Gamma = 1800$ Oe, and $q = 1.00$.

It should be noted that the Tsallis distributions entering into the decomposition of the "standard" spectrum of α-Fe should not be related to real magnetic centers generating them. The decomposition serves only for convenient mathematical representation of the spectrum in order to use it as an individual component in the analysis of more complex spectra.

4. CONCLUSIONS

In this work, it was demonstrated that, for the quantitative description of EMR spectra of magnetic nanoparticles, it is advisable to use the decomposition of the spectrum into components with the line shape described by the Tsallis distribution. An important advantage of the Tsallis distribution curves is a smooth variation in the form with a change in the parameter q. This enables one to decrease the number of components of the decomposition and improve its quality. For relatively narrow and symmetric EMR spectra of nanoparticles, well-known formulas developed for the analysis of polycrystalline spectra of paramagnetic centers can be applied. For the quantitative analysis of broad asymmetric spectra of non-single-phase nanoparticles, it was proposed to use "standard" EPR spectra preliminary obtained in the analysis of nearly single-phase nanoparticles.

ACKNOWLEDGMENTS

The author would like to thank S.P. Gubin, G.Yu. Yurkov, and D.A. Gorin for providing the samples containing magnetic nanoparticles.

This study was supported by the Russian Science Foundation (project no. 14-12-01379) and the Russian Foundation for Basic Research (project no. 15-04-03790)

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Translated by E. Chernokozhin