Super-ferrimagnetism of magnetite nanoparticles in a weak magnetic field

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Abstract. Film composites based on the magnetite Fe₃O₄ nanoparticles in the polyvinyl alcohol matrix were studied by means of the Mössbauer spectroscopy in a weak magnetic field, mainly at room temperature. The Mössbauer spectra in the absence of a magnetic field show a superposition of minor (poor-resolved) magnetic hyperfine structure and major collapsed spectrum typical for superparamagnetic particles. Such a pattern evidences for the mean particles size (\(<D> \approx 4\) nm) being close to the ‘blocking’ size for this material at a given temperature. The spectra taken in a weak (0.34 T) magnetic field show almost complete restoration of the magnetic hyperfine structure characteristic for the nanoparticles of the kind. The experimental Mössbauer spectra have been analyzed within the recently developed three-level relaxation model of magnetic dynamics in an ensemble of single-domain particles. This model takes into account the precession and diffusion of particle’s uniform magnetization as well as the particles size distribution.

1. Introduction
The most important characteristics of single-domain nanoparticles used in magnetic storage media are their magnetization switching time and the strength of corresponding external magnetic field. Typical value of the switching time in modern computers is of about nanosecond which comes into the \(^{57}\)Fe Mössbauer time window defined by the lifetime of excited nuclear level and Larmor precession of nuclear magnetic moments. This is why the Mössbauer spectroscopy allows one to obtain a valuable information in the field. However, up to now the Mössbauer spectra of fine magnetic particles are usually measured as a function of temperature only. Sometimes the spectra are measured in a strong external magnetic field of about several Tesla, which is comparable with the strength of the hyperfine field, \(H_{hf}\), at the nucleus, so that one can roughly estimate only the average saturation magnetization of the sample as a whole. Meanwhile, a substantial influence of weak magnetic fields with the strength of about 0.1 T on the shape of Mössbauer spectra of magnetic nanoparticles has been already observed [1-4], but such investigations have been not systematically performed.
2. Experimental
Polymer film composites containing magnetite nanoparticles were prepared in situ via the alkali hydrolysis reaction of a 2:1 mixture of iron(III) and iron(II) chlorides, respectively. The synthesis procedure was described in detail earlier [5]. Mössbauer spectra were measured with a conventional spectrometer, which operated in the constant acceleration mode for $^{57}$Co(Rh) source with the activity of 10 mCi. Figure 1 shows the typical $^{57}$Fe Mössbauer absorption spectra of iron oxide nanoparticles in a polyvinyl alcohol (PVA) matrix, which were measured in weak magnetic fields. As one can see, a noticeable spectrum change already in a weak external field $H = 0.4$ kOe in comparison with the spectrum at $H = 0$. With the external field increasing a substantial spectra transformation is observed, which contained much of additional information on characteristics of the specimen magnetic dynamics. This effect is similar to that of the field–induced magnetic ordering near the Curie temperature in the bulk ferrimagnetic YIG [6]. An example of the analysis of the spectra field dependence in terms of the DISCVER procedure which allows one to decompose a spectrum into partial sextets with Gaussian broaden lines corresponding to a hyperfine field $H_{hf}$ distribution [7] is shown by solid lines in Figure 1. Formally, this approach describes the restoration of the resolved hyperfine structure corresponding to an effective magnetization of the studied nanoparticles in a magnetic field. However, one should treat somehow the partial sextets evaluated as a function of the field strength. Such a treatment requires to apply a physical model taking into consideration qualitative peculiarities of the nanoparticles magnetization with different orientation relative to the field direction.

3. Results and discussion
A phenomenological model of magnetic dynamics and corresponding relaxation Mössbauer spectra of the nanoparticles in a magnetic field taking into account the magnetic anisotropy, inhomogeneous precession and continuous diffusion of the uniform magnetization vector $\textbf{M}$ was developed in [8]. In a magnetic field with the strength $H$ less than critical value $H_c(\Theta) \ (0.5 H_c < H_c(\Theta) < H_c, \ H_c = 2K/M_0, \ \Theta$ is the angle between the $\textbf{H}$ vector and the easiest magnetization axis, $K$ is the constant of axial magnetic anisotropy, $M_0$ is the low temperature saturation magnetization), the vector $\textbf{M}$ for the given energy

$$E = -K \cos^2 \theta - HM$$

($\theta$ is the angle between the easiest magnetization axis and $\textbf{M}$) describes a conic surface around each of three poles corresponding to two energy local minima and absolute maximum for each nanoparticle. The precession trajectories forms are determined by the Hamiltonian (1). The average value of the magnetization $\bar{M}(E)$ for each orbit is defined by elliptical integrals along the given trajectory as a function of characteristic frequencies of the vector $\textbf{M}$ precession and diffusion as well as of the effective external field

$$h = H / H_c .$$

A three-level relaxation model (TLRM) with stochastic states determined by given average values of the magnetization $\bar{M}_i(H, \Theta, T)$ and the equilibrium populations $\bar{W}_i(H, \Theta, T)$ for three ranges of the $\textbf{M}$ stable rotation around the poles mentioned was developed as a first approximation [8]. Supposing that the vector $\textbf{M}$ relaxation has a diffusion character, i.e., goes through infinitely small rotations, transitions between the states in the local energy minima (1) occur only through the state 3 corresponding to the absolute energy maximum. This approach allows one not only to perform a numerical analysis of the experimental spectra of a single domain particles ensemble in a magnetic field but also to draw at least qualitative conclusions concerning specific spectra shapes realization.
Figure 1. (Left panel) Room-temperature $^{57}\text{Fe}$ Mössbauer spectra (squares) of iron-oxide nanoparticles in a magnetic field $H$ (the field direction is perpendicular to the gamma-beam). The resulting and partial spectra (solid lines) are calculated within the Gaussian hyperfine field distribution [7]. (Right panel) Mössbauer spectra of an ensemble of nanoparticles ($H_{\text{hf}}^{(0)} = 500$ kOe, $K\bar{V} = 500$ K, $K\sigma_V = 400$ K) in a magnetic field, which calculated in the three-level relaxation model with $p_0 = 5$ GHz and $\bar{H}_C = 10$ kOe for different values of $\sigma_h = 0.03, 0.04, 0.13, 0.19, 0.23, 0.35$ (from top to bottom).

Calculations of the Mössbauer spectra within the TLRM can be performed in terms of the stochastic approach [8]. For performing a simultaneous analysis of the spectra measured at different $H$ values it is necessary to fulfil averaging of partial spectra both over particles dimension ($\bar{V}$ and/or $K\bar{V}$) and over a parameter of interaction between particles. In our case we performed the averaging using Gaussian distribution of the particle volume and the effective magnetic field (2) with the corresponding widths $\sigma_V$ and $\sigma_h$. The results of a qualitative analysis of all the series of the
experimental spectra within the “physical” TLRM are shown in Figure 1 (right) where the calculations were performed with the fixed values of \( K \sigma = 500 \), \( K \sigma = 400 \) K and \( H_c = 10 \) kOe for different values \( \sigma_h \). As one can see the shape of all the spectra measured at different strengths of the external field is described satisfactorily within the same set of physical parameters. Especially note a proper description of the “high-temperature doublet” at \( H = 0 \), which has purely “magnetic” origin within the model and is caused by the presence of an average molecular field \( \vec{h} \neq 0 \). Usually the presence of such a doublet is ascribed to the surface iron atoms contribution, the state of which differs from that of the inner atoms due to the electric field gradient acting on nuclei, which results in the excited nuclear level splitting due to a quadrupole interaction.

An analysis of large number of the specimen experimental spectra within the TLRM allows one to make self-consistent estimates of physical characteristics of the material studied. Using the value of the average particles diameter \( \langle D \rangle \approx 4 \) nm known from the X-Ray diffraction study and found average anisotropy energy \( K \sigma = 500 \), one can estimate the average anisotropy constant \( K \approx 2 \times 10^5 \) J/m\(^2\) that in turn allows one to estimate the value of the average particles magnetization \( M_0 \approx 0.5 \) A/m. In our opinion, the estimated value of the critical magnetic field \( H_c \) is the substantially better and universal characteristic of the material studied in comparison with the coercive field value derived from conventional measurements of magnetization curves because the latter depends not only on the material properties but also on external conditions. As for the concrete values of the parameter \( \sigma_h \) characterizing the dispersion of inter-particle interactions they contain also information about the \( K \) distribution over the specimen. In order to extract this information one has to modify slightly the calculation scheme for the next stage of analysis. Here we did not perform a numerical fit of the experimental spectra within TLRM, which in principle permits to fulfil a quantitative analysis, because the procedure used needs a substantial optimization of numerical calculations.

4. Conclusions
The presented approach for simultaneous analysis of Mössbauer spectra of the nanoparticles in a weak magnetic field within the given model of magnetic dynamics of the system studied essentially expands the possibilities of Mössbauer spectroscopy for characterization of nanomagnetic materials. Subsequently we plan to develop this approach for simultaneous analysis of both Mössbauer spectra and magnetization curves within the same relaxation model.

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