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Mössbauer spectroscopy for characterizing biodegradation of magnetic nanoparticles in a living organism

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Abstract We have developed a model for describing nanoparticles magnetic dynamics. This allows us to fit self-consistently the wide set of the experimental data, particularly, the evolution of Mössbauer spectral shape with temperature and external magnetic field as well as the magnetization curves for nanoparticles injected into mice. Thus, we reliably evaluate changes in characteristics of the nanoparticles and their chemical transformation to ferritin-like forms in mouse's organs as a function of time after injection of nanoparticles. Actually, the approach allows one to quantitatively characterize biodegradation and biotransformation of magnetic particles in a body.

Keywords Magnetic nanoparticles · Magnetic dynamics · Biodegradation

1 Introduction

Diverse shapes of the temperature- and field-dependent Mössbauer absorption spectra of magnetic nanoparticles (NP) obviously supplies one with a large amount of information about physical characteristics inherent to NP staying in different environment [1]. With that the longstanding ^{57}Fe Mössbauer spectroscopy is efficiently used to study spin states, electronic and dynamical properties of iron-containing proteins of animals and humans [2].

The main problem in interpreting the Mössbauer spectra of iron-containing NP injected into a living organism is to reliably decompose them into partial subspectra of exogenous iron atoms in NP and endogenous iron atoms [3]. The most adequate

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model for describing the spectra is the multi-level relaxation model that takes into account their magnetic anisotropy and diffusion of uniform magnetization [4]. This model was efficiently used to fit the experimental spectra of an ensemble of magnetic NP at different temperatures, including NP injected into a living organism [3]. One more highly informative technique is based on measurements of the Mössbauer spectra of NP in a weak static magnetic field. A first-approximation theory for describing such spectra has been developed in the recent time [5, 6]. The theory can be extended within the multi-level relaxation model [4] on the basis of a model of magnetic dynamics developed in [5].

The main goal of this contribution is to demonstrate briefly the advantages of the theoretical approach to the self-consistent treatment of the temperature and field-dependent Mössbauer spectra for characterizing the biodegradation and biotransformation of magnetic NP in an organism by the example of behavior of NP injected into a mouse.

2 Samples

We have used commercially available ferrofluid "fluidMAG-ARA-250" (Chemicell Gmbh, Germany). The magnetic NP suspended in PBS were injected intravenously in tails of mice. At different time after the injection, the mice were sacrificed, organs extracted and lyophilized. The dried initial ferrofluid and lyophilized mouse's organs were then grinded and the powder samples were prepared for Mössbauer studies.

3 Relaxation model for describing the experimental data

The multi-level relaxation model for describing the Mössbauer spectra is based on the quantum-mechanical description of NP [4]. Calculations of the Mössbauer spectra within the model can be performed in terms of the stochastic approach according to which the absorption spectrum is described by the general expression [1, 4]:

$$\sigma(\omega) \propto -\mathrm{Im} \sum_{\alpha} |C_{\alpha}|^2 \langle W| \hat{A}_{\alpha}^{-1}(\omega) |1\rangle.$$

Here, $\alpha = (m_e, m_g)$ specifies hyperfine transition with the nuclear spin projections m_e and m_g onto the $\mathbf{H}_{hf}$ direction, C_{α} is the intensity of α-th transition, $\langle W|$ is the row vector of the equilibrium occupation probabilities of the stochastic states, $|1\rangle$ is a column vector with all components equal to unity. The operator $\hat{A}_{\alpha}(\omega)$ is defined by the diagonal matrix of hyperfine interaction and the relaxation matrix specified by the diffusion constant D [4].

The Mössbauer spectra of nanoparticles in a field can be described within a similar stochastic approach with operators of more general type [1, 6]:

$$\sigma(\omega) \propto -\mathrm{Im} \int \sin\Theta d\Theta \sum_{\eta} \mathrm{Sp}\left(\hat{V}_{\eta} \langle W| \hat{\mathbf{A}}^{-1}(\omega, \Theta) |1\rangle \hat{V}_{\eta}^{+}\right).$$

where Θ is the angle between the field direction and the particle's easy axis, $\hat{V}_{\eta}$ is the operator for the interaction of the gamma-quantum with a given polarization η and $\hat{\mathbf{A}}(\omega, \Theta)$ is a superoperator defined by the Liouville operators of hyperfine

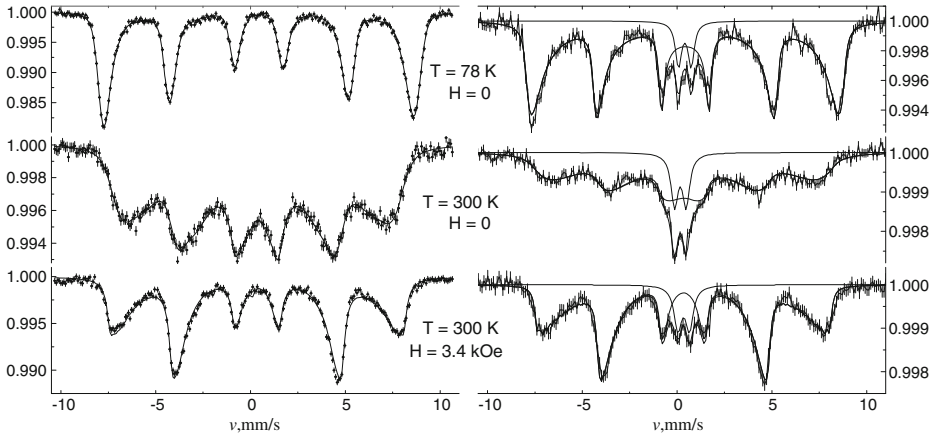

Fig. 1 ^{57}Fe Mössbauer spectra of initial NP (*left panel*) and a mouse liver 2 weeks after NP injection (*right panel*). Solid lines represent partial spectra of NP, calculated within the multi-level relaxation model, and ferritin-like contribution as well as the resulting spectra

interaction for each stochastic state and the relaxation matrix specified by the probabilities of transitions between the states [6].

4 Results

Using the formalism we have managed a least-squares fitting procedure to treat the set of experimental spectra (Fig. 1) and magnetization curves. This allows us to reliably characterize the sample with initial NP with estimates of: the average magnetic anisotropy energy $K\bar{V}/k_{\mathrm{B}} = 350 \pm 40\,\mathrm{K}$, the mean particle diameter $\bar{d} = 10.6 \pm 0.1\,\mathrm{nm}$, the Gaussian width of particle's size distribution $\sigma_d/\bar{d} = 0.21 \pm 0.03$, the critical field of magnetization reversal $H_{\mathrm{C}} = 1.62 \pm 0.08\,\mathrm{kOe}$, the ^{57}Fe concentration $n_{\mathrm{NP}} = (6.3 \pm 0.4) \cdot 10^{18}\ \mathrm{cm}^{-3}$, $D = 0.95 \pm 0.05$ mm/s and $H_{\mathrm{hf}} = 491.5 \pm 0.8$ kOe for $T = 300$ K.

An analogous fitting procedure has been applied to the spectra of the samples of mouse liver at different stages of biodegradation with an inclusion of additional variable parameters of a quadrupolar doublet, describing the contribution of ferritin-like proteins: the partial area, the isomer shift δ_{f}, and the quadrupolar splitting $2q$ [3]. The following principal physical parameters of the sample of mouse liver 2 weeks after NP injection have been evaluated: $K\bar{V}/k_{\mathrm{B}} = 50 \pm 20\,\mathrm{K}$, $\sigma_d/\bar{d} = 0.7 \pm 0.1$, $H_{\mathrm{C}} = 1.18 \pm 0.04$ kOe, $\delta_{\mathrm{f}} = 0.35 \pm 0.02$ mm/s and $2q = 0.60 \pm 0.03$ mm/s for $T = 300$ K.

Also, such an analysis allowed us to evaluate time evolution for NP and 'ferritin' concentrations: $n_{\mathrm{NP}} \cdot 10^{-18}\ (\mathrm{cm}^{-3}) = 5.8 \pm 0.5, 4.7 \pm 0.4, 2.1 \pm 0.3, 1.6 \pm 0.4$, and $n_{\mathrm{f}} \cdot 10^{-18}\ (\mathrm{cm}^{-3}) = 0.07 \pm 0.02, 0.08 \pm 0.01, 0.14 \pm 0.02, 0.63 \pm 0.04$ for the samples of mice sacrificed in 2 hours, 2 days, 2 weeks, 2 months after NP injection, respectively. These values were estimated from the partial spectral areas and recoilless fractions evaluated within the Debye model.

Thus, an analytical technique for characterizing the biodegradation and biotransformation of magnetic NP in an organism is developed and realized on the basis of self-consistent treatment of a minimal set of experimental data including three Mössbauer spectra taken at different temperatures and in a magnetic field as well as the magnetization curve for the sample studied.

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