Mössbauer spectra and magnetization curves of nanoparticles in a weak magnetic field

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Abstract. Magnetic relaxation effects revealed in Mössbauer spectra and magnetization measurements of nanoparticles are discussed in the framework of specific models for magnetic dynamics of an ensemble of single-domain particles, which allow one to treat both the temperature and magnetic field-dependent magnetization curves and Mössbauer spectra in a self-consistent way within the same set of physical parameters inherent to the system studied. Based on the stochastic approaches, a simplified three-level stochastic model taking into account the magnetic anisotropy, precession and diffusion of uniform magnetization of single-domain particles is developed in order to describe the Mössbauer absorption spectra of nanoparticles in a weak magnetic field.

1. Introduction
A number of techniques are applied to study the non-equilibrium magnetism of nanoparticles, among which the most informative seem to be the conventional magnetization measurements and Mössbauer spectroscopy, which obviously supply one with a large amount of information about physical characteristics inherent to the systems studied. The principal difference between these two complementary techniques is that they can probe magnetic properties of the same material in different frequency ranges: the magnetization measurements are carried out at lower frequencies (of about 1–1000 Hz) while Mössbauer spectroscopy can reveal the magnetic dynamics of nanoparticles at higher frequencies due to the Mössbauer time window (10^{-11}–10^{-6} s for ^{57}Fe nuclei).

The only way to extract the reach information from the experimental data is to define a model of the magnetic dynamics in order to describe the whole set of the experimental data for the sample studied. Since a long time two fundamental ideas are used to describe qualitatively the magnetic properties of single-domain fine particles: (i) the Néel’s equation for the relaxation rate between local energy minima of a ferromagnetic particle with the uniaxial magnetic anisotropy energy density $K$ [1]:

$$p = p_0 \exp(-KV/k_BT)$$

where $p_0$ is the fluctuation rate slightly dependent on temperature $T$, $V$ is the particle’s volume, $k_B$ is the Boltzmann constant and (ii) the Stoner-Wohlfarth (SW) model for particles with the uniform magnetization $M_0$ and the energy density in an external magnetic field $H$ [2]:

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\[ E = -K \cos^2(\Theta - \varphi) - HM_0 \cos \varphi \tag{2} \]

where \( \Theta \) and \( \varphi \) are the angles composed by the external field direction with the easiest magnetization axis and the magnetization vector, respectively.

Both the models are widely used in analyzing experimental magnetization curves and Mössbauer spectra of materials with magnetic nanoparticles, however such an analysis actually reduces to estimates of a finite number of empirical parameters such as the blocking temperature \( T_b \) and the coercivity \( H_c \) which are determined not only by the properties (e.g., \( K, V, M_0, \) and \( p_0 \)) of the sample under investigation, but also by the external parameters of the measurement method (external field strength, temperature and their scanning rate, prehistory of the sample, etc.). In such a situation, it is necessary to search for a compromise solution, i.e., to develop a phenomenological model applicable for analyzing the experimental data and estimating the aforementioned parameters of single-domain particles.

2. Generalized Stoner-Wohlfarth model

The main limitation of the original SW model is a very approximate description of the relaxation process that transitions between the states with different energy minima are forbidden until the applied field strength does not exceed the critical value \( H_c(\Theta) \) \[2\]. In accordance with the Néel’s idea and equation (1), a more accurate description of the relaxation process within the SW model has been suggested under the assumption that the relaxation process is specified by only two parameters \[3, 4\]:

\[ p_{12,21}(H,\Theta,T) = p_0 \exp\left[-\left(E_{\text{max}}(H,\Theta) - E_{1,2}(H,\Theta)\right)/k_BT\right] \tag{3} \]

where \( E_{\text{max}}(H,\Theta) \) and \( E_{1,2}(H,\Theta) \) are the energies of the local maxima and minima, which are evaluated by simple numerical calculations from equation (2).

When temperature or applied field is changed in time, the actual populations of the local states \( w_1(t) \) and \( w_2(t) \) of each particle with a given \( \Theta \) are non-equilibrium and can be determined using the differential equation for their difference \( \tilde{w}(t) = w_1(t) - w_2(t) \) \[4\]:

\[ d\tilde{w}(t)/dt = -p(t)[\tilde{w}(t) - \tilde{w}_0(t)] \tag{4} \]

where \( p(t) = p_{12}(t) + p_{21}(t) \) and

\[ \tilde{w}_0(t) = \tanh\left[\frac{[E_2(H,\Theta) - E_1(H,\Theta)]V}{2k_BT}\right] \tag{5} \]

is the difference of equilibrium populations at instantaneous values of \( H \) and \( T \) depending on time \[5\].

The time evolution of the magnetization of particles with the given angle \( \theta \) is defined by \[4\]

\[ M(t,\Theta) = M_0\left(1 + \tilde{w}(t,\Theta)\right)\cos \varphi_1(\Theta) + (1 - \tilde{w}(t,\Theta))\cos \varphi_2(\Theta)\right)/2. \tag{6} \]

Then, the total magnetic moment of an ensemble of the randomly oriented and non-interacting SW particles can be calculated by averaging equation (6) over \( \Theta \). One can see that the simple differential equation (4) appears to be universal in describing temperature- and field-dependent magnetization curves measured by any experimental technique (either conventional magnetization measurements or Mössbauer spectroscopy) at arbitrary measuring frequency, field strength and temperature \[3, 4\].

3. General theory of stochastic reorientation of particle’s magnetization

The main limitation of the original and generalized SW models is that thermal excitations at local energy minima are not taken into account. The general theory of the stochastic reorientation of the vector \( \mathbf{M} \) for the statistical ensemble of ferromagnetic single-domain particles in the presence of a rapidly fluctuating chaotic field \( \mathbf{h}(t) \) has been developed under the assumption that the stochastic process \( \mathbf{h}(t) \) is stationary and isotropic \[6\] followed by a differential equation for the probability density (population) \( W(\theta,\phi) \) of states with a given \( \mathbf{M} \) direction and the relaxation operator \[6, 7\]:
where \( D \) is the diffusion constant and \( \gamma \) is the gyromagnetic ratio. However, in spite of a number of simulations based on this equation, a real numerical analysis of the experimental data on the temperature- and field-dependent magnetization has not been yet performed within this approach due to first of all computational problems.

Recently, an alternative approach for describing the magnetic dynamics of an ensemble of single-domain particles in a magnetic field has been proposed [5], in which the magnetization precession orbits are considered as stochastic states of each particle, the states (orbits) with a given energy being characterized by the mean magnetization value determined by the curved integrals along the corresponding trajectory \( C_E \):

\[
\overline{M}_{z,x}(\Theta,E) = \int M_{z,x} dm / \overline{\Omega}_E(\Theta,\varphi) \left( \int dm / \overline{\Omega}_E(\Theta,\varphi) \right)^{-1}
\]

where \( \overline{\Omega}_E(\Theta,\varphi) = \Omega_E^2(\Theta,\varphi) + p_E^2(\Theta,\varphi) \) is the instantaneous angular velocity and \( p_E(\Theta,\varphi) \) is the predetermined probability of transition per unit time from the given trajectory \( C_E \) at the point \((\Theta,\varphi)\) to the adjacent trajectories \( C_{E \pm \Delta E} \) [5]. Based on this approach, a general model of magnetic dynamics can be determined for calculating the magnetic characteristics in various measurement methods and analyzing numerically the experimental data.

One can write down also the general expression for the Mössbauer absorption spectrum in this representation using the conventional stochastic approach [3, 8-10]:

\[
\sigma(\omega,\Theta) \propto \text{Im} \sum_\eta \text{Sp} \left( V_\eta W | A^{-1}(\omega,\Theta) | 1 \right) V_\eta^+
\]

where \( V_\eta \) is the operator for the interaction of the gamma-quantum with a given polarization \( \eta \) and the nucleus, \( W \) is the row vector of the equilibrium occupation probabilities of the stochastic states, \( | 1 \) \) is a column vector with all components equal to unity. The superoperator \( A(\omega,\Theta) \) is defined by the Liouville operators of hyperfine interaction specified by the Hamiltonians in the ground and excited states for each stochastic state \( i \) [9]:

\[
H_i^{\text{g,e}} = -g_{\text{g,e}} \mu_N H_{\text{hf}}^{(0)} \text{M}_i^{\text{g,e}} / M_0
\]

and the relaxation matrix specified by the probabilities \( p_i(\Theta,\varphi) \) [5].

4. Mössbauer spectra of nanoparticles in a magnetic field within three-level relaxation model

However, the main problems of such an analysis within the multi-level relaxation model are associated with the optimization of a calculation procedure. This is why a simplified three-level stochastic model taking into account that the vector \( \text{M} \) for a given energy \( E \) describes a conic surface around one of the three poles corresponding to two local minima and the absolute maximum of energy (2) has been introduced in order to describe the Mössbauer absorption spectra of nanoparticles in a weak magnetic field [9]. Indeed, a similar three-level relaxation model has been already introduced as a formal intermediate step in passing from the Neel’s two-level model to a multi-level model in the absence of a field [10]. Moreover, the physical reason for correctness of the three-level model results actually from the fact that the kinetic equation with the relaxation operator (7) is reduced to the Schrödinger equation with just a three-well potential even in the absence of a field [7].

The three-level relaxation model is valid under the condition \( \Gamma_0 / h << D << \Omega_0 = 2\gamma K / M_0 \) (\( \Gamma_0 \) is the width of the excited nuclear level) and takes into account physical mechanisms of formation of the
magnetic hyperfine structure for nanoparticles in a weak (as compared to the hyperfine field) magnetic field [9]. A number of typical Mössbauer absorption spectra calculated within this model for the field direction composing the ‘magic’ angle with the gamma-beam (in order not to mix weak field and polarization effects) can be found in [9]. Here, figure 1 shows $^{57}$Fe Mössbauer absorption spectra calculated within the three-level relaxation model for various values of the transverse and longitudinal external field as well as of the efficient energy barrier $KV/k_BT$ and just demonstrates the polarization effects.

Figure 1. $^{57}$Fe Mössbauer spectra of an ensemble of nanoparticles ($\mu_0H_{hf}^{(0)} = 50$ T, $p_0 = 3$ GHz) in a transverse (solid lines) and longitudinal (points) magnetic field, which calculated in the three-level relaxation model as a function of the effective energy barrier $KV/k_BT=0.5$ (left column), 2 (right column) and the normalized field strength $h=HM_0/2K=0.01, 0.1, 0.5, 1, 2$ (from bottom to top).

Thus, the three-level relaxation model taking into account the magnetic anisotropy, precession and diffusion of uniform magnetization can be efficiently used to describe the Mössbauer absorption spectra of an ensemble of magnetic nanoparticles in a weak magnetic field, e.g., measured long ago [11, 12], but not simulated yet. Applications of the model for analyzing the experimental Mössbauer absorption spectra of magnetic nanoparticles are presented in the contributions of Polikarpov et al. in this issue.

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