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# Quantum Model of the Magnetic Dynamics of Single-Domain Particles for Describing Their Magnetization Curves and Mössbauer Spectra in a Weak Magnetic Field

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**Abstract**—A universal approach to describing the equilibrium magnetization curves and relaxation Mössbauer spectra of magnetic nanoparticles is proposed for consistent analysis of magnetometry and gamma-resonance experimental data, based solving a quantum-mechanical problem for a particle with spin $S$ that has intrinsic magnetic anisotropy and is positioned in an external magnetic field.

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## INTRODUCTION

The interest in magnetic particles and clusters with sizes on the order of several nanometers (i.e., single-domain particles and clusters) is due primarily to their high abundance and application in different materials, devices, processes, and technologies (e.g., ferrofluids, magnetic and magnetooptical devices for recording data, color imaging devices, NMR tomography, chemical catalysis, biotechnological production, and the magnetic delivery of drugs). This dictates the need for systematic research on the structural and magnetic properties of such materials, both for optimizing the processes of their synthesis and revealing specific features of magnetism in systems of nanometer particles.

The most informative ways of studying the magnetic dynamics of nanoparticles are making standard measurements of the magnetization of test samples and gamma resonance (Mössbauer) spectroscopy, which are often used in research on the structural, magnetic, and thermodynamic properties of nanocrystalline magnetic materials.

These methods differ in many respects and complement each other. Magnetometry provides the absolute value of the total magnetic moment of a sample, and is thereby a direct but integral method. In Mössbauer spectroscopy, the sensors of interaction are the atomic nuclei of a resonance isotope, which reflect the local pattern of intra-atomic fields; however, these so-called hyperfine fields are only an indirect reflection of the macroscopic fields inside a crystal. Magnetic measurements almost always require the application of an external field to a studied system and detecting its response to this action. This greatly complicates theoretical analysis of the results, due to the superimposition of a system's internal processes and the external disturbance. At the same time, measuring the magnetic characteristics of a substance by means of gamma resonance does not require an external source of the field; it is replaced by the strong internal fields of the material's own atoms, which turns out to be a great advantage in studying the complicated magnetic dynamics of small particles. Magnetic curves are recorded in slowly changing fields with frequencies ranging from mHz to kHz, which determine the characteristic durations of measurement. The sensitivity of Mössbauer spectroscopy to dynamic processes is limited on one hand by the natural widths of the resonance lines and by the Larmor precession of nuclear spins in a hyperfine magnetic field on the other; for the most abundant isotopes, this lies in the frequency interval between MHz and GHz.

We have recently been developing a unified formalism for describing the magnetization curves [1, 2] and gamma resonance spectra [2, 3] of magnetic nanomaterials that depends on temperature and the external magnetic field, with allowance for the interaction between resonance nuclei and inhomogeneous environmental electric fields [4]. The aim of this work is to demonstrate the effectiveness of the new approach through the example of diagnostics of the commercial

ferrofluid ARA-250 (Chemicell GmbH, Germany) [5], which is used in biological and medical applications [6].

## ANALYSIS OF MÖSSBAUER SPECTRA

Samples for our Mössbauer investigations were prepared by drying the initial ferrofluid, a water suspension of polymer globules with implanted nanoparticles of magnetite $Fe_3O_4$. The polymer coating prevented particle aggregation in both the initial ferrofluid and liophilized samples. Mössbauer absorption spectra of the $^{57}$Fe nuclei, plotted using a standard spectrometer in the constant acceleration mode in the range of temperature $T$ from nitrogen boiling to room temperature are displayed in Fig. 1.

The temperature evolution of the experimental data qualitatively repeats the transformation of gamma-resonance absorption curves in the multilevel model of the magnetic dynamics of single-domain particles in [7], which we used to describe our experiment (see Fig. 1). Table 1 presents the nanoparticle characteristics obtained from a joint analysis of a number of spectra: the height of the energy barrier of intrinsic magnetic anisotropy $KV_0$ (where $K$ is the anisotropy constant and $V$ is the particle volume), which is uniform over the range of temperatures and corresponds to the central value of the Gaussian distribution of the number of particles over diameters with the relative width $\gamma_d$; temperature dependence of the rate of diffusion $D$ of particles magnetic moments; and the Mössbauer parameters (viz., the hyperfine fields on resonance nuclei $H_{hf}$ and shifts $\delta$ of the spectra's centers of gravity).

Note first of all the satisfactory quality of our theoretical description over the studied range of temperatures. The obtained value of anisotropy energy $KV_0$, which exceeds 300 K, corresponds to a "strongly magnetic" state of particles up to room temperature. The spread of particle sizes $\gamma_d$ of around 0.3 is also quite realistic. The growth of diffusion constant $D$ along with temperature agrees with the commonly assumed temperature dependence of the intensity of the Brownian process. The reduction in hyperfine field

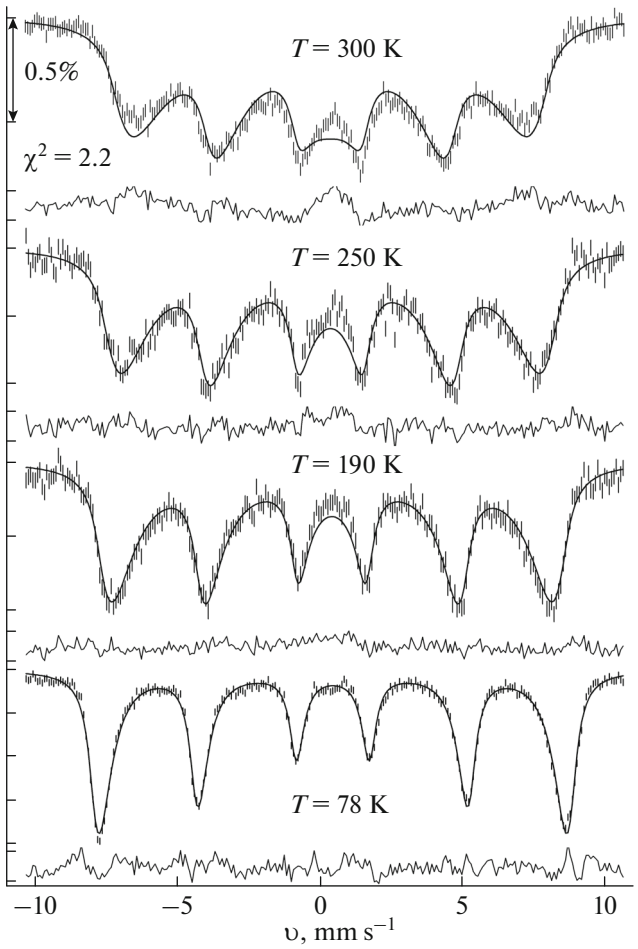


**Fig. 1.** Experimental Mössbauer spectra (vertical bars) of $^{57}$Fe nuclei in the sample of ARA-250 nanoparticles at different temperatures, along with theoretical curves (solid lines) calculated using the multilevel model of the magnetic dynamics of single-domain particles.

**Table 1.** Parameters of ARA-250 nanoparticles at different temperatures $T$, reconstructed from their Mössbauer spectra in the multilevel model of the magnetic dynamics of single-domain particles: anisotropy energy $KV_0$ for the center of the Gaussian distribution of the number of particles over diameters with relative width $\gamma_d$, resonance line broadening in the absorber $\Delta\Gamma_a$, diffusion constant $D$, hyperfine field on a nucleus $H_{hf}$, and total spectrum shift $\delta$

| $T$, K | 300 | 250 | 190 | 78 |
|---|---|---|---|---|
| $KV_0$, K | 360 (20) | | | |
| $\gamma_d$ | 0.31 (2) | | | |
| $\Delta\Gamma_a$, mm s$^{-1}$ | 0.23 (1) | | | |
| $D$, MHz | 11.5 (5) | 7.2 (6) | 5.7 (8) | 2.5 (6) |
| $H_{hf}$, kOe | 496 (2) | 512 (2) | 523 (2) | 528 (1) |
| $\delta$, mm s$^{-1}$ | 0.349 (8) | 0.359 (8) | 0.411 (7) | 0.444 (2) |

**Table 2.** Parameters of ARA-250 nanoparticles, reconstructed using the multilevel model of the magnetic dynamics with allowance for combined hyperfine interaction: $KV_0$, $\gamma_d$, $D$, $H_{hf}$, and $\delta$ are similar to the ones listed in Table 1, along with quadrupolar interaction constant $q$

| $T$, K | 300 | 250 | 190 | 78 |
|---|---|---|---|---|
| $KV_0$, K | 370 (10) | | | |
| $\gamma_d$ | 0.28 (1) | | | |
| $q$, mm s$^{-1}$ | −0.34 (1) | | | |
| $D$, MHz | 12.7 (5) | 8.9 (6) | 7.7 (8) | 13 (2) |
| $H_{hf}$, kOe | 501 (2) | 517 (2) | 527 (1) | 530 (1) |
| $\delta$, mm s$^{-1}$ | 0.352 (8) | 0.366 (8) | 0.414 (7) | 0.448 (2) |

$H_{hf}$ on atomic nuclei as the temperature rises reflects the wane of the saturation magnetization $M_0$ of particles, due to heat disordering of the magnetic moments of the atoms that constitute them. When a sample is frozen down to liquid nitrogen temperature, its spectrum's center of gravity $\delta$ shifts by natural line width $\Gamma_0$, reflecting the universal temperature shift of gamma resonance due to the quadratic Doppler effect.

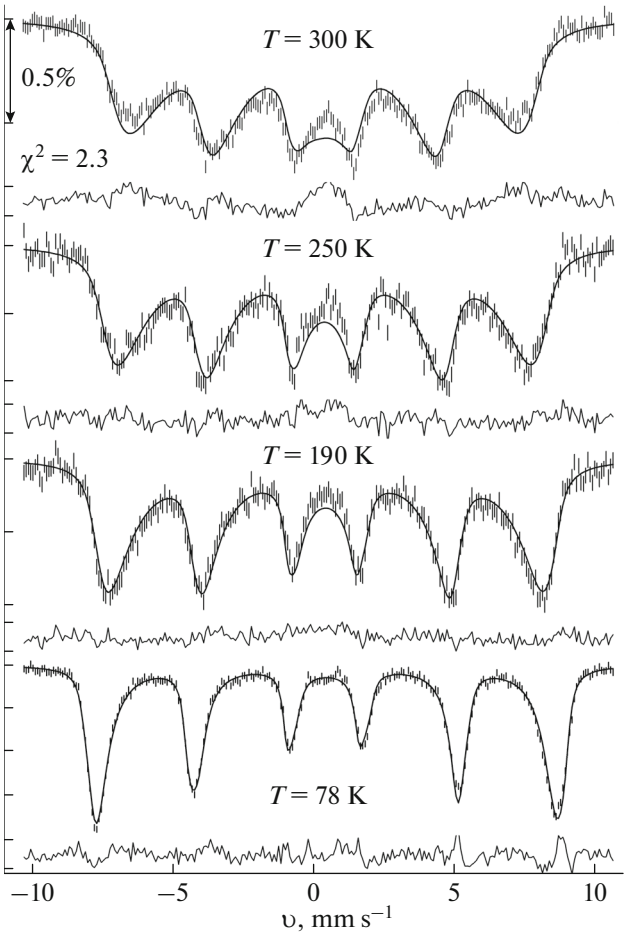


**Fig. 2.** Experimental and theoretical spectra of ARA-250 nanoparticles at different temperatures, calculated using the multilevel model of magnetic dynamics with allowance for electric quadrupolar interaction.

However, a major problem of the above approach is the need to introduce broadening of resonance line $\Delta\Gamma_a$ in the absorber, which exceeds the natural value $2\Gamma_0$ (see Table 1). Additional width of the Mössbauer line can appear as a result of the interaction between the quadrupolar moment of resonance nuclei and the electric field gradient in the area of their locations; for surface atoms under the conditions of broken crystal symmetry, it can differ from zero. To verify this assumption, we tried describing the same experimental data in the multilevel model of magnetic dynamics that was generalized in [4] to combined hyperfine interaction in the system. The results from our analysis are presented in Fig. 2. Corresponding parameters $KV_0$, $\gamma_d$, $D$, $H_{hf}$, and $\delta$, along with quadrupolar interaction constant $q$, which is the same for all temperatures, are listed in Table 2.

At first glance, the coincidence of the results of analysis using models with different level of completeness (see Figs. 1 and 2) is even somewhat confusing. However, more careful consideration does reveal a marked difference between the descriptions of spectrum "tails", which testifies in favor of the physical approach. Among the required parameters, the temperature dependence of diffusion coefficient $D(T)$ turns out to be most sensitive to a change in model: it is transformed from a direct proportionality into a constant, which is quite possible due to the indefiniteness of the microscopic specification of the relaxation parameter. The value of the diffusion coefficient at room temperature remains almost invariable, as do the values of the macroscopic characteristics (anisotropy energy $KV_0$ and particle size spread $\gamma_d$, which coincide in the both approaches within the margin of experimental errors).

## ANALYSIS OF FIELD SPECTRA

In addition to the widely used way of studying the magnetic properties of small particles based on the temperature evolution of their Mössbauer spectra, we

propose another no less informative way of measuring gamma resonance curves in weak magnetic fields. Its main advantage is the possibility of making measurements only at room temperature, without using expensive means of refrigerating; however, models of magnetic dynamics in the presence of an external field must be used to interpret the data from such measurements.

Figure 3 shows the experimental curves for the resonance absorption of the same ARA-250 nanoparticles, taken in an external magnetic field perpendicular to a beam of gamma-quanta with different values of magnetizing force $H$. To interpret the data, we used a quantum model of the magnetic dynamics of single-domain particles in the quasi-classical approximation for relaxation [3]. In the model, three branches of a continuous Brownian process for the particle magnetization vector are selected in the vicinity of two mimina and one maximum of the energy. We used values of common parameters $KV_0$, $\gamma_d$, and $\Delta\Gamma_a$ consistently obtained from a temperature series of spectra and varied quantities $D$, $H_{hf}$, and $\delta$, which were introduced independently for each temperature point. We also determined the values (individual for each field spectrum) of relative internal field $h_{in}$ in the sample to specify the structure of the energy levels of a magnetic particle in the field. The results from simultaneous analysis of the field series of spectra are presented in Fig. 3, and the resulting values of the model parameters are given in Table 3.

The high quality of the theoretical description of field spectra is immediately apparent, and is even somewhat unexpected for the minimalistic model that we used. It is also pleasant to note the consistency of the obtained values of the varied parameters (diffusion constant $D$, hyperfine field $H_{hf}$, and shift $\delta$ of the center of gravity when $T = 300$ K), and of the corresponding values determined via temperature series analysis. At the same time, the dependence of internal field $h_{in}$ on applied magnetizing force $H$ is much more pronounced than would be expected if we assume there is weak interaction among the ensemble particles. This is easy to see even hen visually analyzing the experimental curves from the strong polarization effects, even for the lowest value of external field $H$: 400 Oe.

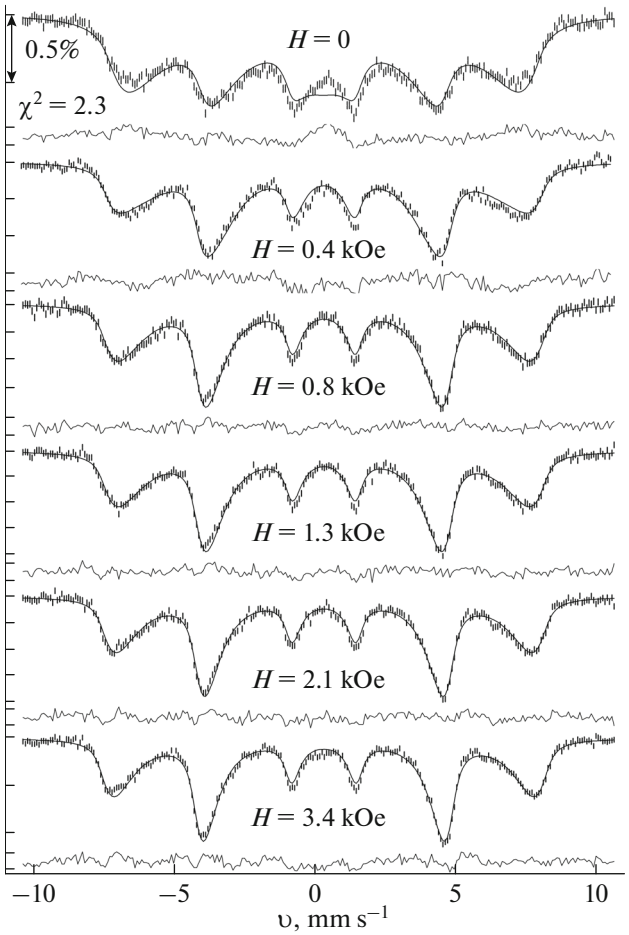


**Fig. 3.** Experimental and theoretical spectra of ARA-250 nanoparticles in the transversal magnetic fields of different magnetizing forces, calculated using the quantum model of magnetic relaxation in a quasi-classical approximation.

**Table 3.** Parameters of ARA-250 nanoparticles in the transverse magnetic fields of different magnetizing forces $H$, reconstructed from their Mössbauer spectra in the quantum model of magnetic relaxation: $KV_0$, $\gamma_d$, $\Delta\Gamma_a$, $D$, $H_{hf}$, and $\delta$ are similar to the ones listed in Table 1, along with relative internal field $h_{in}$ in the sample

| $H$, kOe | 0 | 0.4 | 0.8 | 1.3 | 2.1 | 3.4 |
|---|---|---|---|---|---|---|
| $KV_0$, K | 360 (10) | | | | | |
| $\gamma_d$ | 0.31 (1) | | | | | |
| $\Delta\Gamma_a$, mm s$^{-1}$ | 0.23 (1) | | | | | |
| $D$, MHz | 12.3 (5) | | | | | |
| $H_{hf}$, kOe | 497 (1) | | | | | |
| $\delta$, mm s$^{-1}$ | 0.345 (2) | | | | | |
| $h_{in}$ | – | 0.95 (1) | 1.33 (2) | 1.29 (2) | 1.50 (2) | 1.67 (3) |

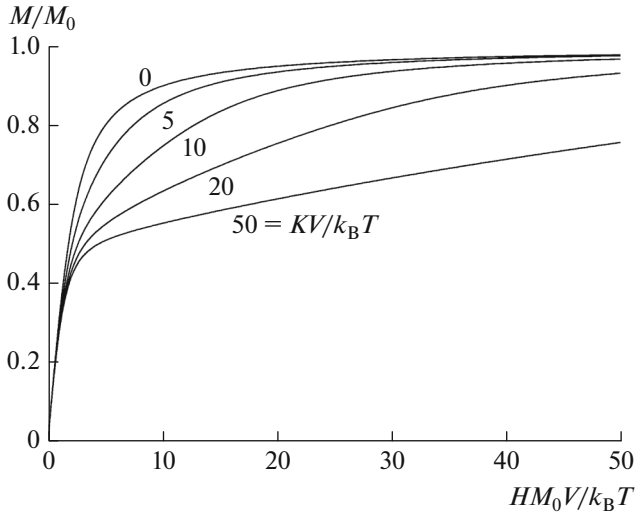


**Fig. 4.** Equilibrium magnetization curves of ferromagnetic nanoparticles, calculated using the quantum model of magnetic relaxation with chaotic orientation of their easy axes for different values of the intrinsic magnetic anisotropy of particles in the classical limit.

## CONCLUSIONS

The intensification of polarization effects in the Mössbauer spectra of nanomagnets when an external field is applied could theoretically be due to an increase in sample magnetization as a result of the dipole interaction among magnetic particles. As direct calculations show [8], however, such effects are rather weak and could hardly result in the registered abrupt increase of internal fields in a studied system of weakly interacting particles. If the combined hyperfine interaction in the presence of an external field is allowed for correctly, we should arrive at some adjustments to the obtained values of the energy parameters. By analogy with the pure case of the intrinsic magnetic anisotropy of particles, however, we would expect that such an improvement of the theoretical description would basically be reduced to a physical interpretation of the broadening of resonance lines but would not appreciably affect their intensity, and therefore not have a great effect on the parameters of the energy scheme.

In our opinion, the most natural explanation for the observed pattern lies in the specific thermodynamics of ferrimagnetic nanoparticles, which cannot be reduced to mere excitations of the total magnetic moment of a particle but allows for sublattice magnetization deviations from mutually opposite orientations. Quantum-mechanical calculations of the structure of energy levels of a ferrimagnetic particle under a presumed finite force of exchange coupling between two magnetic sublattices [9] shows that the density of its stationary states grows rapidly as the energy rises. At the same time, these are the same excited high-energy states that are most sensitive to the action of an external disturbance. We would therefore expect that the effect a field has on a nanocrystalline ferrimagnet would be more pronounced than that on a ferromagnet of the same size, which is apparent from the increase in the effective internal field in the simplified interpretation of ferrimagnetism in the universal model of single-domain particles.

At the same time, the quantum model of magnetic relaxation in [3] should be very useful in describing data from magnetometry measurements, which reflect the response to the external actions of the total magnetic moments of particles. For example, calculations for the thermodynamic properties of nanoparticles ensembles performed with this model in the limit case of large particle macrospins ($S \to \infty$) reveal the universal Langevin behavior of the equilibrium magnetization curves of nontextured samples in weak fields (Fig. 4); this could serve as theoretical justification of the widely used method of estimating average sizes of nanoparticles from the initial inclination of their magnetization curves. In addition, allowing for stochastic transitions between the steady states of magnetic nanoparticles should serve as a basis for quantitatively describing dynamic effects in their systems that are determined not only by current values of the temperature and external field but by their rates of change as well.

## ACKNOWLEDGMENTS

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