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Quantum-Mechanical and Continual Models of the Magnetic Dynamics of Antiferromagnetic Particles in Analyzing Mössbauer Spectra

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Abstract—Recently developed quantum-mechanical and continual models of the magnetic dynamics of antiferromagnetic particles are used to analyze the temperature series of Mössbauer spectra of nanoparticles based on trivalent iron oxide Fe_2O_3. The advantages of the new models are compared and possible generalizations are discussed on the basis of concrete experimental data.

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INRODUCTION

Magnetic nanoparticles based on iron oxides acquire increasingly greater value as nanotechnology continues to develop. These materials are widely used in nature, easily synthesizable under laboratory and industrial conditions, and nontoxic; this allows us to use them as functional bases in biological and medicine applications. Extending the sphere of application of magnetic nanomaterials requires constant improvement in the ways and means of their diagnostics, which is a separate scientific and technical problem. Electron microscopy allows us to control the sizes and shapes of obtained particles, but it is insensitive to the chemical composition and magnetic ordering of the substances under study. X-ray procedures, which are widely used to characterize bulk materials, often provide little information on finely dispersed powders due to the strong broadening of diffraction peaks from nanosize grains. Chemical (and particularly histological) methods allow us to establish the presence of iron of a specific valence, but they cannot answer the question of the quantitative content of one or another phase.

High-resolution gamma-resonant spectroscopy, which has been used successfully to investigate both bulk and nanocrystalline materials for the last fifty years, thus acquires special value. First of all, the record narrow width of the resonant line allows us to distinguish the hyperfine structure of nuclear levels (which is determined by intra-atomic and crystalline fields, and therefore the valences of absorbing atoms and their chemical environment) so that the spectral contributions from different compounds can be separated and their absolute magnitudes used to estimate the concentrations of corresponding phases. Second, along with the short decay time of the excited state of the nucleus, which is comparable to the characteristic relaxation rates in systems of small particles, the specific distributions of the hyperfine parameters that appear upon moving from bulk samples to nanocrystallites allow us to observe the size and dynamic effects characteristic of the objects under study.

Finally, in contrast to macroscopic characteristics averaged over a sample, Mössbauer spectroscopy's sensitivity to local fields in areas where resonant nuclei are found makes it a powerful tool for studying the magnetic structure of matter. However, adequate theoretical models that consider the specific thermodynamic and magnetic properties of studied systems must be developed to extract the rich information contained in the experimental Mössbauer spectra of magnetic nanocomposites.

Over the last few years, we have developed a formalism suitable for describing gamma-resonant spectra of both ferromagnetic [1–3] and antiferromagnetic [4–6] particles. The main aim of this work is to demonstrate the effectiveness of our new approaches using diagnostics of nanoparticles of trivalent iron oxide Fe_2O_3 as an example.

EXPERIMENT AND PRELIMINARY ANALYSIS

The synthesis of iron oxide nanocrystals in a dextran shell was described in detail in [7], which was devoted to their comprehensive experimental investigation via electron microscopy, magnetometry, NMR spectroscopy, and gamma-resonant spectroscopy. The main problem encountered by the researchers was

preparing virtually monodispersed tiny particles. The transmission electron microscopy data, which found a narrow spread of diameters of magnetic nuclei that peaked near 3 nm, indicates the authors of [7] attained the desired result. The scientists' subsequent efforts focused on investigating the magnetic behavior of an ensemble of synthesized ultrafine particles. Assuming initially that they were dealing with ferrimagnetic crystals of γ-Fe_2O_3 maghemite, the authors of [7] interpreted the evolution of the Mössbauer spectra from a well-resolved magnetic sextet at low temperatures to a clearly pronounced quadrupole doublet at high temperatures as a relaxation transition from the frozen-in spin state to the superparamagnetic state. Along with indirect data on the nuclear magnetic resonance on hydrogen atoms in a polymer shell, they treated direct measurements of magnetic susceptibility in dc and ac fields in the same terms. The difficulties in describing the behavior in the system and its deviation from the type expected were in this case attributed to the presence of disordered outer layers in the particles and the effect of interparticle interaction.

Wanting to verify their conclusions, the authors of [7] turned to us with a proposal to perform a quantitative analysis of their Mössbauer data and kindly placing them at our disposal. These data, which were already partially published in the above article, are presented in Fig. 1. As the theoretical base for a simultaneous analysis of the temperature series of the spectra, we selected the familiar multilevel model of the magnetic dynamics of single-domain particles [1], generalized for the presence of quadrupole interaction in the system [2]. In addition to such characteristics of hyperfine interactions as contact Coulomb interaction δ, magnetic dipole interaction H_{hf}, and electric quadrupole interaction q, the key parameters of this representation are the characteristic magnetic anisotropy energy, specified by product KV (where K is the anisotropy constant and V is the particle volume) and diffusivity D, determined by the intensity of the stochastic relaxation process. The results from processing with this model are presented in Fig. 1, while the reconstructed values of parameters are presented in Table 1.

However, our analysis shows that the standard relaxation model is not enough to describe the totality of the spectra even upon virtually independent processing: while the low-temperature measurements can be explained in terms of the selected approach if we allow for variations in the temperature of anisotropy energy KV and the high-temperature weakly resolved structure can be formally ascribed to an abrupt increase in diffusivity D, the shape of the experimental curves in the intermediate temperature range does not match the selected theoretical scheme and requires the introduction of an additional central component. This contribution is described in Fig. 1 by an extra

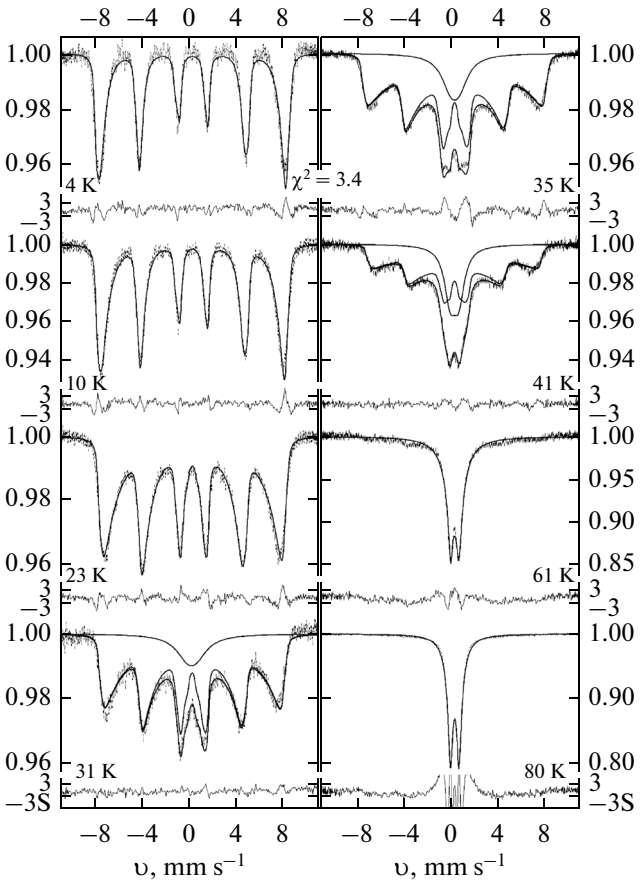

Fig. 1. Experimental Mössbauer spectra of Fe_2O_3 nanoparticles at different temperatures, adjusted for absorber thickness (vertical strokes), and theoretical spectra (solid lines) calculated using the multilevel model of the magnetic dynamics of single-domain particles with an additional contribution from weakly magnetic states. S—experimental error

doublet of broadened lines with splitting $2q$, while its parameters are presented in Table 1. In addition, it is noteworthy that the relaxation processes in most cases play no appreciable role ($D = 0$) and traces of the resolved magnetic structure are retained even in high-temperature spectra, indicating that their mechanisms of formation differ from those of relaxation. Note too that the introduction of the particle-size distribution does not improve the quality of description, thereby indirectly confirming the high monodispersity of the particles under study.

These results lead us to believe that we are dealing here with macroscopic quantum effects of repopulation of the particles' energy levels with different values of the magnetic moment that are often observed in nanoparticles of weakly magnetic materials and have recently found a theoretical interpretation, rather than with the temperature transition of strongly magnetic particles into the superparamagnetic state [4–6], and

Table 1. Parameters of Fe_2O_3 particles at different temperatures T, reconstructed using the experimental Mössbauer spectra and the multilevel model of the magnetic dynamics of single-domain particles with an additional contribution from weakly magnetic states

T, K	4	10	23	31	35	41	61	80
q, mm s^{-1}	0.3655 (3)							
D, mm s^{-1}	0						10.3 (1)	16.3 (1)
KV, K	38.2 (7)	69.9 (7)	78.7 (4)	73.2 (17)	55.9 (8)	40.3 (16)	0	
H_{hf}, kOe	507.7 (3)	502.0 (2)	491.4 (2)	486.8 (5)	484.6 (3)	460.9 (8)	430	400
δ, mm s^{-1}	0.326 (3)	0.330 (2)	0.336 (2)	0.322 (5)	0.340 (3)	0.366 (7)	0.340 (2)	0.327 (1)
σ	2.84 (2)	3.06 (1)	2.95 (1)	2.34 (2)	2.51 (1)	2.04 (1)	2.59 (1)	2.822 (2)
δ_d, mm s^{-1}				0.25 (5)	0.32 (1)	0.30 (1)		
Γ_d, mm s^{-1}				2.4 (2)	1.9 (1)	1.2 (1)		
σ_d				0.33 (1)	0.47 (1)	0.76 (1)		

The column on the left lists quadrupole interaction constant q common to both components and all temperatures; diffusivity D; energy barrier in anisotropy field KV; largest hyperfine field on an iron nucleus H_{hf}; isomer shifts δ and δ_d; and effective absorber thicknesses σ and σ_d for the principal and additional components, respectively; and total line width of effective doublet Γ_d. Root-mean-square errors in the last digit are shown in parentheses.

that the samples under study are, despite all expectations, an antiferromagnetic modification of trivalent iron oxide: or hematite α-Fe_2O_3. The main section of this work is devoted to verifying this assumption.

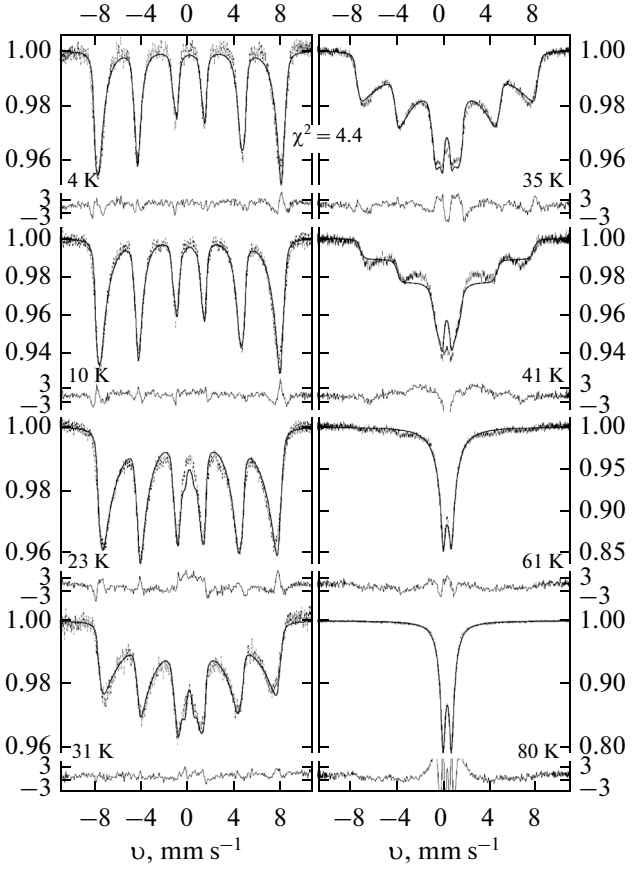

Fig. 2. Experimental and theoretical spectra calculated using the continual model of the magnetic dynamics of antiferromagnetic particles.

ANALYSIS USING ANTIFERROMAGNETIC MODELS

To analyze the available experimental data, let us initially use the simplest macroscopic model of ideal antiferromagnetic particles [6] based on solving equations of motion for the magnetization of two sublattices. Assuming the axial symmetry of the solution, these equations define the four normal modes of the self-consistent and uniform precession of magnetization vectors around the easy axis of a particle. The excitation spectrum of two fundamental modes is qualitatively similar to the energy spectrum in the standard model of ferromagnetic particles [1] and is determined by anisotropy energy KV, while the third branch makes a comparable contribution only to the states with minor projections of the magnetic moment onto the symmetry axis (as a rule, the fourth mode lies much higher in terms of energy and plays no substantial role). The relationship between the principal and additional branches is specified by exchange interaction energy A, while the relaxation process, allowing for branching, can be determined so that we are able to quantitatively characterize it by diffusivity D, as was done in [1].

The results from our analysis according to this model are presented in Fig. 2, and the corresponding parameters are presented in Table 2. Let us first note the satisfactory agreement between the theory and experiment over virtually the entire temperature range and the similarity between the values of hyperfine parameters and those found at the preliminary stage of analysis. As before, processing in this case shows that the relaxation mechanisms are in fact excluded from the number of main factors of spectrum formation, while the strong drop in the anisotropy energy arises for the reason that the barrier between the lowest energy levels for the primary antiferromagnetic

branches is almost twice as high as the one for the ferromagnetic branches.

The suppression of relaxation in the ensemble of antiferromagnetic particles is scarcely surprising, since it depends on the dipole–dipole interactions between the total magnetic moments of the particles, which are smaller by several orders of magnitude in antiferromagnets than in ferromagnets and ferrimagnets. It is therefore natural to try to create a theory of antiferromagnetic particles that though ignores stochastic processes but makes no a priori assumptions regarding the properties of the sought solution. We developed such a theory in [4, 5] based on quantum-mechanical substantiation of a problem with two spins of magnetic sublattices associated by exchange interaction and located in an axial magnetic anisotropy field. We use here its simplest variant for the case of equivalent spins [4]. Calculations using this model represent a solution of the complete eigenvalues problem for a two-spin Hamiltonian in the basis of eigenfunctions of the total momentum and its projection. Wave functions corresponding to different projections of the total momentum are orthogonal, which in combination with the tridiagonal structure of the density matrix greatly simplifies the calculations, making them feasible for a personal computer.

The results from data processing with the quantum model of thermodynamics are presented in Fig. 3, and our values of the parameters are presented in Table 3. It is noteworthy that the absence of relaxation mechanisms leads to a notable transformation of the high-temperature curves, but the quality of description remains quite satisfactory over the entire temperature range, while the shape of these curves itself partially explains the resolved magnetic structure, which appears in spectra at high temperatures. Due to the more rigid computational schematic, the model parameters are then precisely determined from the experiment with no partial a priori specification, though the obtained values in some cases differ from those found using relaxation models.

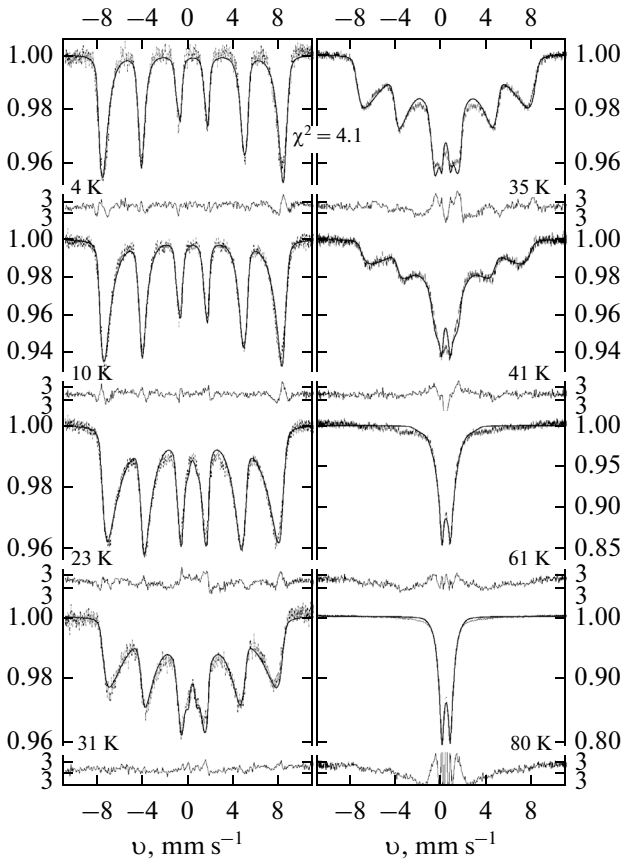

Fig. 3. Experimental and theoretical spectra calculated using the quantum-mechanical model of the thermodynamics of antiferromagnetic particles.

Table 2. Parameters of Fe_2O_3 nanoparticles, reconstructed using the continual model of the magnetic dynamics of antiferromagnetic particles: exchange energy A common to all temperatures as well as parameters similar to those presented in Table 1 for the principal component

T, K	4	10	23	31	35	41	61	80
A, K	760 (40)							
q, mm s^{-1}	0.3647 (3)							
D, mm s^{-1}	0						9.7 (1)	15.0 (1)
KV, K	20.1 (4)	38.4 (4)	48.3 (4)	37.1 (5)	24.3 (3)	0		
H_{hf}, kOe	507.3 (3)	501.2 (2)	488.7 (2)	486.7 (5)	486.1 (3)	466.0(10)	430	400
δ, mm s^{-1}	0.326 (3)	0.330 (2)	0.335 (2)	0.321 (5)	0.337 (2)	0.315 (5)	0.340 (2)	0.327 (1)
σ	2.85 (1)	3.08 (1)	2.86 (1)	2.61 (1)	2.94 (1)	2.89 (1)	2.59 (1)	2.818 (2)

Table 3. Parameters of Fe_2O_3 nanoparticles, reconstructed using the quantum-mechanical model of the thermodynamics of antiferromagnetic particles and similar to those presented in Table 2, excluding diffusivity

T, K	4	10	23	31	35	41	61	80
A, K	180 (1)							
q, mm s^{-1}	0.3525 (4)							
KV, K	38.9 (3)	75.2 (4)	99.9 (4)	91.4 (4)	80.9 (2)	60.5 (3)	15 (1)	12 (1)
H_{hf}, kOe	512.3 (2)	507.9 (2)	497.8 (2)	497.3 (5)	496.1 (3)	474.8 (9)	180 (4)	100 (1)
δ, mm s^{-1}	0.326 (3)	0.331 (2)	0.336 (2)	0.323 (5)	0.338 (2)	0.326 (4)	0.343 (2)	0.328 (1)
σ	2.80 (2)	3.07 (1)	2.91 (1)	2.61 (1)	2.92 (1)	2.80 (1)	2.29 (1)	2.491 (2)

CONCLUSIONS

The difference between the results produced by the macroscopic and quantum models requires explanation and poses the question of selecting the preferable description. The main difficulty of continuous consideration lies in the initial limitation on the class of desired solutions in the form of the orbits of uniform precession, which does not include nutation-type motions. The problem of completeness does not arise in the quantum model, and the absence of a dynamic description for antiferromagnets should not be critical. This allows us decide in favor of the discrete representation. Consideration of the distribution with respect to the uncompensated spin, which does not change the description in general but makes it more realistic, could also turn out to be important [5]. Finally, the introduction of an additional contribution to the energy of anisotropy, which we selected in the simplest one-parameter form, can lead to better agreement between parameters reconstructed at different temperatures.

At the same time, we believe that even the results found using the simplest physical models are convincing evidence of the antiferromagnetic behavior of the investigated system. Many of the measurements performed by the authors of [7] (e.g., of weak saturation magnetization or the high resonant frequencies characteristic of antiferromagnetic samples in particular) give evidence in favor of this hypothesis. However, it should be noted that the question of the magnetic ordering in ultrafine particles is very difficult [8], and in order to arrive at a final conclusion both in the case above and in many other disputable instances, we require not only the improvement of the models of antiferromagnetism but the development of a valuable theory of ferrimagnetic particles.

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