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Macroscopic quantum effects observed in Mössbauer spectra of antiferromagnetic nanoparticles

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Abstract The ^{57}Fe Mössbauer spectra of antiferromagnetic nanoparticles have been measured for almost half a century and often displayed a specific (non-superparamagnetic) temperature evolution of the spectral shape which looks like a quantum superposition of well-resolved magnetic hyperfine structure and single line or quadrupolar doublet of lines with the temperature-dependent partial spectral areas. We have developed a quantum-mechanical model for describing thermodynamic characteristics of an ensemble of ideal and "uncompensated" antiferromagnetic nanoparticles with uniaxial magnetic anisotropy in the first approximation of slowly relaxing macrospins of magnetic sublattices. This model allows one to qualitatively describe the macroscopic quantum effects observed in the Mössbauer spectra and to clarify principally the difference in thermodynamic properties of ferromagnetic and antiferromagnetic particles revealed in spectroscopic measurements.

Keywords Antiferromagnetic nanoparticles · Mössbauer spectroscopy · Magnetic dynamics · Macroscopic quantum phenomena

1 Introduction

For the last half a century a number of the Mössbauer spectra were collected on materials containing fine particles of different magnetic nature [1–4]. The vast majority of the absorption spectra independent of the particles magnetic nature display qualitatively the same evolution of the spectral shape with temperature changing: a well-resolved hyperfine magnetic structure, i.e. sextet of lines for ^{57}Fe nuclei,

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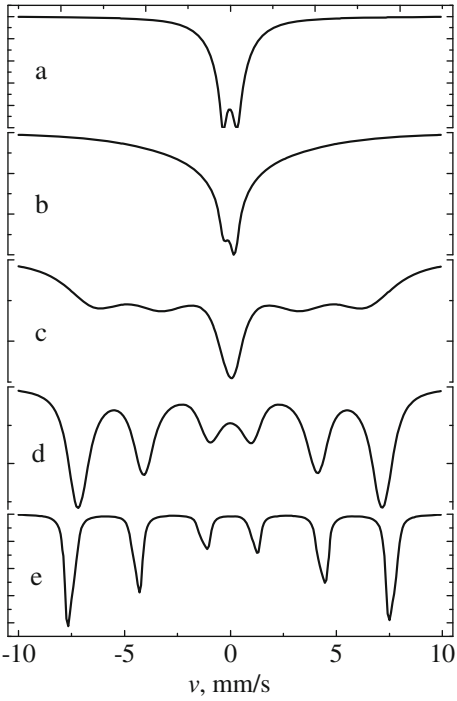

Fig. 1 ^{57}Fe Mössbauer absorption spectra of an ensemble of single-domain FM particles, calculated within the multi-level relaxation model [5, 6] at $D = 1$ GHz and $KV/k_BT = 0.1, 2, 4, 6, 10$ (**a–e**). Hereafter, $H_{hf} = 500$ kOe and $q = 0.35$ mm/s

observed at lower temperatures gradually transforms through a broaden hyperfine structure at intermediate temperatures to the collapse of the hyperfine structure into a single line or a quadrupolar doublet of lines at higher temperatures (Fig. 1). This universal transformation of the spectral shape is usually treated in the framework of the simplest two-level relaxation model for single-domain ferromagnetic (FM) particles [5, 6] based on the Néel's relaxation of homogeneously magnetized FM particles with uniaxial magnetic anisotropy (superparamagnetism) [7]. In order to take into account thermal excitations inside the local energy wells of magnetic anisotropy more refined multi-level relaxation models have been developed [5, 6, 8] and extended for describing the Mössbauer spectra of nanoparticles in a magnetic field [9, 10]. These models are efficiently used for evaluating the experimental spectra of magnetic nanoparticles [11–13].

At the same time, a principally different kind of the temperature evolution of the spectral shape has been observed exceptionally for antiferromagnetic (AFM) nanoparticles long ago [1] and multiply repeated later [4, 14–16]. The collapse of a low-temperature well-resolved hyperfine magnetic structure into a single line or a quadropolar doublet of lines at high temperature is not accompanied by a 'conventional' line broadening at intermediate temperatures, all the spectral lines remain narrow in the whole temperature range and only the partial weights of the well-resolved hyperfine magnetic structure and the single line or the quadropolar doublet of lines change gradually with temperature increasing (Fig. 2). Such a spectral transformation evidences for the quantum nature of the effect because it testifies first of all about the temperature-dependent populations of well-defined energy states, the ground one with a large value of the effective hyperfine field at

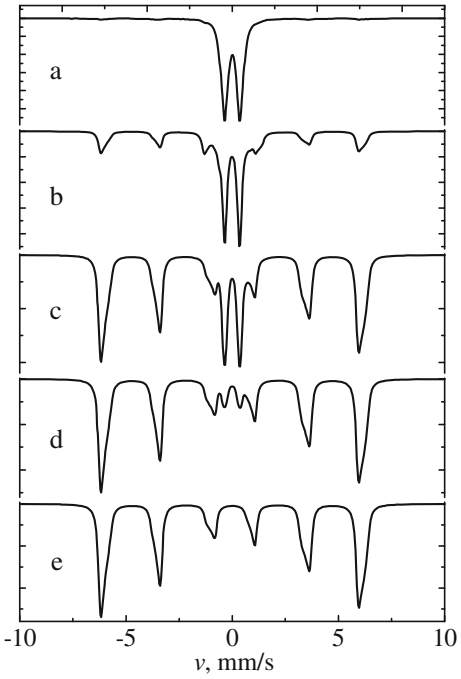

Fig. 2 ^{57}Fe Mössbauer spectra of an ensemble of ideal AFM particles with $S = 100$, $k = 0.001$ and $KV/k_B T = 0.1, 1, 2, 4, 10$ (**a–e**), calculated in the slow relaxation limit, $D << \Gamma_0$ (see text)

nuclei, H_{hf}, and an excited state or states with a small or zero H_{hf} value providing that magnetic relaxation processes are slow enough. A proper explanation of the behavior has been given recently in terms of macroscopic quantum phenomena in AFM nanoparticles [17–19].

In this contribution we will discuss the principles and problems of the theoretical approaches for describing the Mössbauer spectra of non-ferromagnetic nanoparticles including the abovementioned macroscopic quantum effects observed in the absorption spectra of AFM nanoparticles.

2 Thermodynamics of ideal AFM nanoparticles

Magnetic properties of AFM nanoparticles have been considered on a phenomenological level by Néel in terms of uncompensated magnetic moments on two magnetic sublattices (superantiferromagnetism) [20]. This idea has been widely explored for describing magnetization curves of AFM particles [21–23] and in studies of macroscopic quantum phenomena in small AFM particles [24, 25]. However, the ground state of AFM nanoparticles is much more complicated as compared to that for a bulk sample, which is evidenced from the atomic-scale magnetic modeling [26]. Moreover, relaxation processes should occur even for an ideal AFM nanoparticle and resemble those for an ensemble of FM particles in the first approximation whereas the presence of an uncompensated magnetic moment results in a slight distortion of the idealized pattern [17, 19]. This requires a proper theory to be developed for analyzing experimental data and characterizing real materials containing nanoparticles.

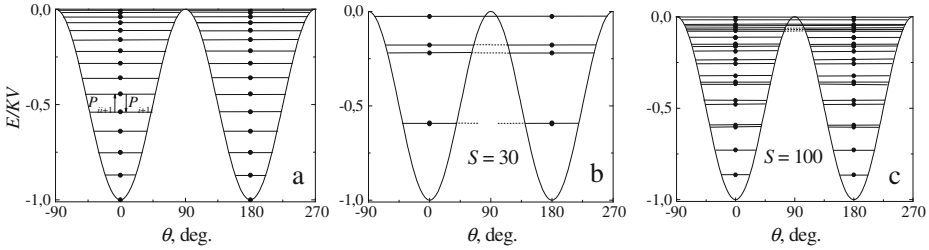

Fig. 3 Schemes of the energy levels of a FM particle (**a**) and the lowest-lying energy levels of ideal AFM particles with $S = 30$ (**b**) and 100 (**c**) for $k = 0.01$

The simplest possible model for describing thermodynamic properties of an ensemble of ideal AFM nanoparticles with uniaxial anisotropy has been recently developed within the Hamiltonian in the two magnetic sublattices approximation [17, 19]:

$$\hat{H} = \frac{A}{S(S+s+1)}\left[\hat{\mathbf{S}}_1\hat{\mathbf{S}}_2 - \frac{k}{2}\left(\hat{S}_{z1}^2 + \hat{S}_{z2}^2\right)\right]. \tag{1}$$

Here, A is the renormalized exchange interaction constant ($A > 0$), $\hat{\mathbf{S}}_i$ is the spin operator for i-th magnetic sublattice, $\hat{S}_{zi}$ is the operator of its projection onto the easy axis, $k = KV/A$, $K$is the magnetic anisotropy constant, $V$is the particle volume, $S_1 = S_2 = S, s = 0$. The presence of uniaxial magnetic anisotropy in the Hamiltonian (1) removes the degeneration of the multiplet states with definite values of the total spin M and, however, does not admix the states with different values of the total spin projection m. In this case the stationary particle's states can be described by the eigenvalues $E_j^{(m)}$ and eigenfunctions $\Psi_j^{(m)}$ of the Hamiltonian (1), which can be rather easily calculated (see [17, 19]).

The schemes of the energy levels for a FM particle and low-lying energy levels for AFM particles within the effective macroscopic energy barrier KV are shown in Fig. 3. A qualitative difference in the energy level schemes for FM and AFM nanoparticles is clearly seen in the figure. In the case of ferromagnetism ($A< 0$) the ground FM state represents actually a quasi-continuous spectrum independent of the K value. Due to this circumstance, one can use the macroscopic model of continuous magnetization diffusion [27] for describing magnetic and thermodynamic properties of FM nanoparticles while a quantum-mechanical description is preferable mainly for optimizing computational procedures [3, 5, 6, 8–10].

The situation is drastically different for AFM nanoparticles ($A > 0$) because the scheme of the energy level splitting for AFM particles depends significantly on particular values of the anisotropy constant K and the spin S (Fig. 3). The pressing point here is a smooth transition from the strong coupling of the sublattice magnetizations $\mathbf{S}_1$ and $\mathbf{S}_2$, when a value of k (or K) for a given S value is small enough, to the weak coupling of the sublattice magnetizations, when the k values for a given S value are large enough for forming weakly-split (quasi-degenerate) doublets of energy levels attributed to the wave functions localized in different energy wells. Such a transition between two regimes for the lowest-lying pairs of the

adjacent energy levels with a definite m value is formally characterized by a critical scaling parameter [17, 19]

$$\beta_{1,2}^{(m)} = \frac{kS^2}{m+1}. \tag{2}$$

The strong coupling regime is realized at $\beta_{1,2}^{(m)} << 1$ and the weak coupling of the sublattice magnetizations is observed at $\beta_{1,2}^{(m)} >> 1$. There are only few energy levels in the range of the macroscopic energy wells for S and k values small enough, e.g., five energy levels for $S = 30$ and $k = 0.01$ with only two the lowest levels corresponding to the weak coupling regime (Fig. 3). The number of energy levels in the range of the macroscopic energy wells increases with S increasing. For instance, due to scaling relation (2), the energy schemes for two pairs of values $S = 30$, $k = 0.01$ and $S = 100$, $k \approx 0.001$ are almost identical.

3 Mössbauer spectra of ideal AFM nanoparticles

In order to calculate experimentally observed characteristics, in particular, the Mössbauer spectra, in the framework of the scheme, we will stay within the simplest, but physically justified limiting case of slow magnetic relaxation when the rates of relaxation transitions between the energy levels for an AFM particle are much lower as compared to the characteristic frequency of sublattice magnetization precession. In this case the equilibrium state of an ensemble of AFM nanoparticles can be characterized by the mean spin values for each stationary state

$$\bar{S}_j^{(m)} \equiv \bar{S}_{j1}^{(m)} = \bar{S}_{j2}^{(m)} = \pm \left\langle \Psi_j^{(m)*} \middle| \hat{S}_z \middle| \Psi_j^{(m)} \right\rangle \tag{3}$$

and by the corresponding populations of the states for a given temperature T

$$W_j^{(m)} = \frac{\exp\left(-E_j^{(m)}/k_{\mathrm{B}}T\right)}{\sum\limits_{n,i} \exp\left(-E_i^{(n)}/k_{\mathrm{B}}T\right)}. \tag{4}$$

Then, the Mössbauer spectra of an ensemble of AFM nanoparticles in the presence of quadrupolar hyperfine interaction can be described by the formalism with averaging over the random orientation of the easy magnetization axis that composes an angle Θ with the principal axis z' of the electric field gradient at the nucleus [5, 6, 19]. The cross-section for absorption of a gamma-quantum with energy $E_\gamma = \hbar\omega$ can be expressed for ^{57}Fe nuclei in a rather simple form:

$$\sigma(\omega) = \sigma_{\mathrm{a}} \sum_{j,m} W_j^{(m)} \int \sin\Theta d\Theta L\left(\omega, \Theta, \bar{S}_j^{(m)}/S\right). \tag{5}$$

Here, σ_{a} is the effective absorber thickness,

$$L(\omega, \Theta, x) = -\frac{\Gamma_0}{6} Im \sum_{\eta} \sum_{\substack{m_{\mathrm{g}} m_{\mathrm{e}} \\ j, \tilde{m}_j}} \frac{C_{m_{\mathrm{g}} m_{\mathrm{e}} \tilde{m}_j}}{\tilde{\omega} - \tilde{\lambda}_j(\Theta, x) - x\omega_{\mathrm{g}} m_{\mathrm{g}} + i\Gamma_0/2}, \tag{6}$$

$$C_{m_{\mathrm{g}} m_{\mathrm{e}} \tilde{m}_j} = V_{m_{\mathrm{g}} \tilde{m}_j}^{(\eta)+} \left\langle m_{\mathrm{e}} \mid \tilde{m}_j \right\rangle V_{m_{\mathrm{e}} m_{\mathrm{g}}}^{(\eta)}, \tag{7}$$

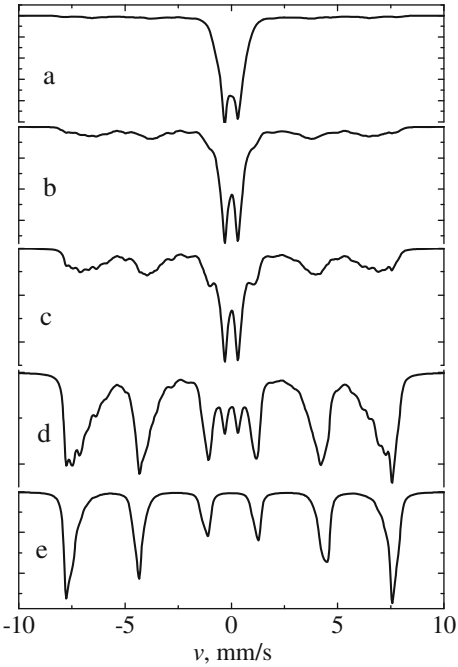

Fig. 4 ^{57}Fe Mössbauer spectra of an ensemble of ideal AFM particles with $S = 100$, $k = 0.01$ and $KV/k_{\mathrm{B}}T = 0.1, 1, 2, 4, 10$ (**a–e**)

$\Gamma_0 \equiv \Gamma_0/\hbar$ is the width of the excited nuclear level in frequency units, $\tilde{\omega} = \omega - E_0/\hbar$, E_0 is the energy of the resonance transition, m_{g} and m_{e} are the nuclear spin projections onto the hyperfine field direction for the ground (g) and excited (e) nuclear states, $V^{(\eta)}_{m_{\mathrm{e}}m_{\mathrm{g}}}$ are the matrix elements for the operator of interaction of the gamma-quantum with polarization η and the nucleus, the sum over random polarizations for an ensemble of particles is reduced to that over $\eta = x, y, z$ [6, 10],

$$\omega_{\mathrm{g,e}} = -g_{\mathrm{g,e}}\mu_{\mathrm{N}}H_{\mathrm{hf}}/\hbar, \tag{8}$$

$g_{g,e}$ are the nuclear g-factors, μ_{N} is the nuclear magneton, $\tilde{\lambda}_j(\Theta, x)$ are the eigenvalues of the Hamiltonian of combined magnetic and quadrupolar hyperfine interaction for the excited state

$$\hat{H}^{(\mathrm{e})}(\Theta, x) = x\omega_{\mathrm{e}}\hat{I}^{(\mathrm{e})}_z + q\left[\hat{I}^2_{z'} - \frac{1}{3}I_{\mathrm{e}}(I_{\mathrm{e}}+1)\right], \tag{9}$$

$I_{\mathrm{g}} = 1/2$ and $I_{\mathrm{e}} = 3/2$ are the nuclear spins, $\hat{I}^{(\mathrm{e})}_z$ is the operator of spin projections onto the $\mathbf{H}_{\mathrm{hf}}$ direction, q is the constant of quadrupolar interaction, $\hat{I}_{z'}$ is the operator of the nuclear spin projection onto the direction of the axis z', $\tilde{m}_j \equiv \tilde{m}_j(\Theta, x)$ are the nuclear spin projections onto the quantization axis for which the operator representing the Hamiltonian (9) is diagonal. As clearly seen from (5), (6), (8) and (9), the spectral lineshape is principally defined by values of the reduced hyperfine field

$$\bar{H}^{(j,m)}_{\mathrm{hf}} = \frac{\bar{S}^{(m)}_j}{S}H_{\mathrm{hf}}. \tag{10}$$

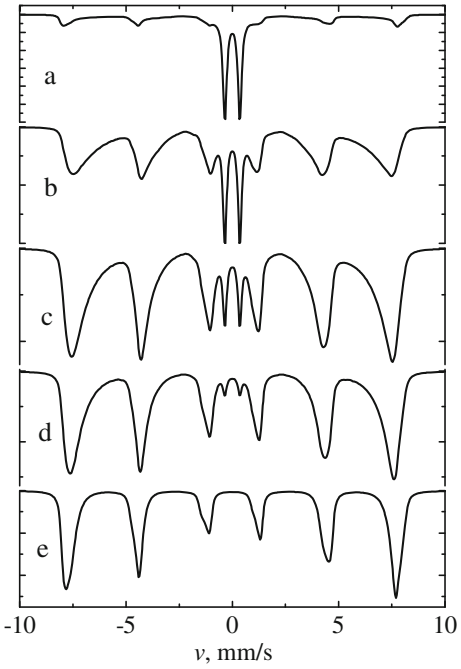

Fig. 5 ^{57}Fe Mössbauer spectra of an ensemble of ideal AFM particles with $S = 1000$, $k = 0.001$ and $KV/k_BT = 0.5$, 2, 3, 4, 10 (**a–e**)

Using (1), (3)–(9), one can calculate the Mössbauer absorption spectra of an ensemble of slowly-relaxing ideal AFM nanoparticles for arbitrary values of model parameters A, K,S, V and H_{hf} at a given temperature. Typical ^{57}Fe spectra calculated within the model for AFM nanoparticles with $S = 100$, $k = 0.001$ and 0.01 are shown in Figs. 2 and 4 as a function of the effective energy barrier KV/k_BT. The spectra demonstrate qualitatively a gradual collapse of a well-resolved hyperfine magnetic structure at low temperature into a quadrupolar doublet at very high temperature, which is not accompanied by a 'conventional' relaxation broadening of lines at intermediate temperatures (like that in Fig. 1) and repeatedly observed in the experimental Mössbauer spectra [1, 4, 14–16]. A quantum nature of the effect is evidenced by the temperature-controllable changes in the populations of a ground state (quasi-degenerate doublet or doublets of energy levels) with a large value of the effective hyperfine field $\bar{H}_{hf}^{(j,m)}$ and excited states (quasi-symmetrical and thus delocalized) with a small value of $\bar{H}_{hf}^{(j,m)}$ providing that magnetic relaxation processes between them are slow enough. Indeed, the presence of scaling in the energy level splitting schemes specified by (2) evidences for the effect to be observed (and have been already observed) in the Mössbauer spectra of AFM nanoparticles with different sizes and not just for very small AFM particles.

When the particles size and/or the magnetic anisotropy K increase, the energy spectrum of an AFM particle tends asymptotically toward a quasi-continuous one displaying a strongly asymmetric shape of spectral lines with sharp outer fronts and inner fronts strongly smeared to the center of the spectrum (Fig. 5). Such a transformation is characteristic for the Mössbauer spectra of FM nanoparticles in the slow relaxation limit [5, 6, 12]. This fact explains fractionally the 'universal'

temperature evolution of the spectral shape observed in the experiments on magnetic nanoparticles of different magnetic nature. However, such a similarity is only seeming because the density of energy states for FM and AFM nanoparticles are essentially different even in the case of quasi-continuous energy spectrum of an AFM particle (Fig. 3). The very effect of a gradual collapse of a low-temperature well-resolved hyperfine magnetic structure into a quadrupolar doublet at high temperature is obviously non-superparamagnetic in character. Its superposition with the strongly asymmetric line shape can principally simulate the 'relaxation' transformation of Mössbauer spectra typical for FM particles. This fact obviously requires for reconsidering and re-evaluating the whole set of experimental spectra collected so far on non-ferromagnetic nanoparticles in a more accurate way.

4 Mössbauer spectra of uncompensated AFM nanoparticles

Thermodynamics of uncompensated AFM particles can be described in the framework of the same Hamiltonian (1) with the uncompensated spin s, $S_1 = S + s$ and $S_2 = S$. Similar to the case of ideal AFM particles discussed before, the presence of the axial magnetic anisotropy eliminates degeneracy of the states with certain values of M, but does not mix the states with different values of the projection of total spin $m$onto the anisotropy axis according to Hamiltonian (1). This essentially simplifies the calculation of the energy levels of an AFM particle for arbitrary values of S and s [18]. The informal difference from the case of ideal AFM particles is determined by the different characters of expansion of wave functions

$$\Psi_j^{(m)} = \sum_i c_{ji}^{(m)} \psi_i^{(m)} \tag{11}$$

by the basis functions [18]

$$\psi_i^{(m)} \equiv \psi_{m_1,m_2}^{(m)}. \tag{12}$$

Typical schemes of the splitting of the energy levels of an AFM particle with $S = 100$ and $s = 0$, 1.5 and 3 as functions of the magnetic anisotropy constant are shown in Fig. 6. Similar to the case of ideal AFM particles, the most important here is the transition from the regime of a strong coupling of the magnetic moments of the sublattices, when the values of k are sufficiently small and the terms with different values of M do not intersect to the weak coupling regime when for sufficiently large values of k a characteristic fine structure of the low-lying levels forms. In all cases, for the specified values of S and s at small k, only a few levels hit the region of the macroscopic energy barrier and, as k is increased, the number of levels in the under-barrier region grows (Fig. 6). The lowest levels are always strongly localized and correspond to a weak coupling regime and with increasing energy the levels delocalize so that the transition to the strong coupling regime occurs [19].

In the slow magnetic relaxation limit, analogously to (3), the stationary states (11) can be characterized by the average values of the spin for each ith sublattice

$$\bar{S}_{ji}^{(m)} = \pm \left\langle \Psi_{ji}^{(m)*} \middle| \hat{S}_{zi} \middle| \Psi_{ji}^{(m)} \right\rangle. \tag{13}$$

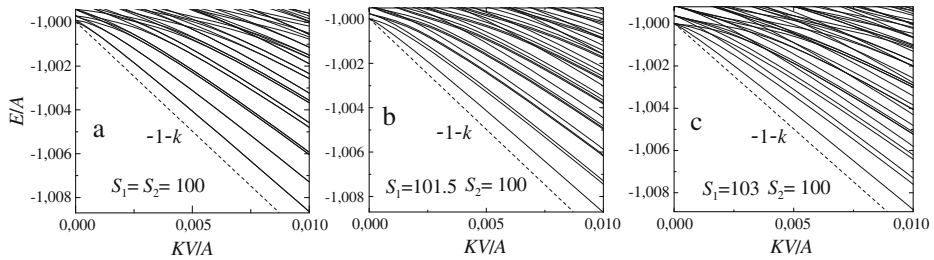

Fig. 6 Schemes of the lowest-lying energy levels splitting as a function of the reduced magnetic anisotropy constant $k = KV/A$ for AFM particles with $S = 100$ and $s = 0$ (**a**), 3/2 (**b**), and 3 (**c**). The dashed lines indicate changes in the effective energy barrier KV/A

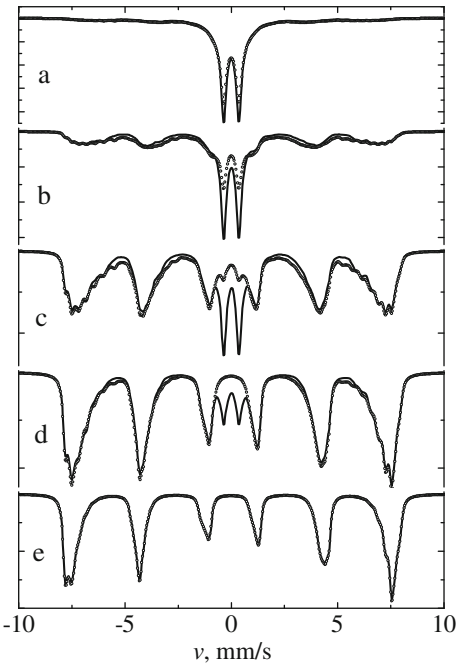

Fig. 7 ^{57}Fe Mössbauer spectra of an ensemble of AFM particles with $S = 100$, $k = 0.01$ and $s = 5/2$ (*circles*), and 3 (*solid lines*) for $KV/k_B T = 0.5, 2, 3, 4, 10$ (**a–e**)

whereas the equilibrium populations of the states are again defined by (4). One can find small values $\bar{S}_{ji}^{(m)}$ for the "symmetric" states in the strong coupling regime, the sharp growth of these values at the break of the coupling between the magnetic moments of the sublattices up to saturation of $\bar{S}_{ji}^{(m)}$ for the strongly "localized" states in the weak coupling regime, and scaling of these characteristics in accordance with parameter $\beta_j^{(m)}$ [18].

Now, one can calculate the Mössbauer spectra of an ensemble of slowly relaxing uncompensated AFM nanoparticles by the same (5)–(9), where he should replace $\bar{S}_j^{(m)}$ by $\bar{S}_{ji}^{(m)}$ and make additional summation by i. Typical spectra of the ensemble of AFM nanoparticles with $S = 100$ and $s = 0$, 5/2, and 3 are shown in Fig. 7. They display the above-mentioned features of the formation of the energy scheme for AFM nanoparticles and qualitatively demonstrate the experimentally observed

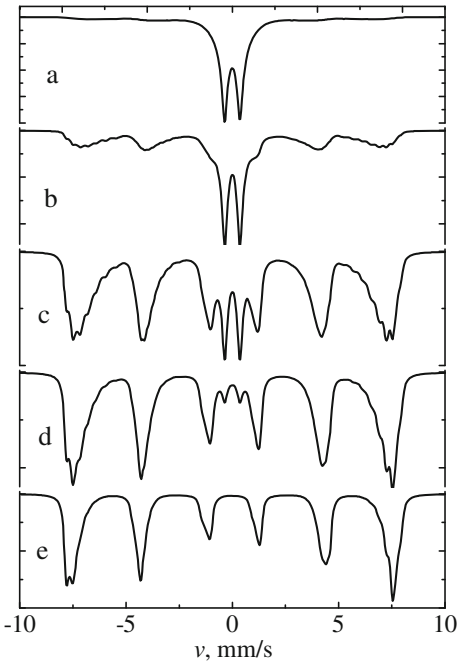

Fig. 8 ^{57}Fe Mössbauer spectra of an ensemble of AFM particles with $S = 100$, $k = 0.01$ and $KV/k_BT = 0.5, 2, 3, 4, 10$ (**a–e**) for the Gaussian distribution of s with mean value $\bar{s} = 0$ and width $\Delta s = 3$

gradual transition from the low-temperature well-resolved hyperfine magnetic structure to the high-temperature quadrupole doublet of lines [1, 14–16].

The presence of the uncompensated spin does not change principally the qualitative character of the temperature evolution of the spectra, but modifies the shape of the spectra to some extent and the characteristic temperature of the transition from the effective magnetic sextet to the doublet of lines. The quantum nature of this effect for arbitrary values of $S$and $s$is caused by the temperature variation in the populations of the low-lying "localized" states with a large H_{hf} value and the higher-lying "delocalized" states with a small H_{hf} value [18] under the sufficiently slow relaxation condition. To describe the spectra of real samples, it is necessary to take into account the spread in s for the ensemble of AFM particles. Figure 8 shows the Mössbauer spectra of the ensemble of AFM nanoparticles calculated by the described scheme with averaging over the Gaussian probability function of $s$with the average value $\bar{s} = 0$ and the width Δs.

5 Conclusions

Thus, the quantum-mechanical model for slowly relaxing macrospins of magnetic sublattices of AFM nanoparticles clarifies the principal difference in thermodynamic behavior of FM and AFM particles. This approach can be easily generalized for describing ferrimagnetic nanoparticles within a similar treatment of the Hamiltonian (1) in terms of multiplet states expanded in the basis functions (12) for unequal spins $S_1 \neq S_2$. The situation becomes naturally more complicated (like that for FM nanoparticles [3, 9, 10]) since for an arbitrary **H** direction the multiplet states

(11) with different values of m are generally admixing. However, in the most informative case of nanoparticles in a magnetic field weak as compared to the effective exchange field a generalization of the formalism derived above can be performed in terms of the perturbation theory. Actual directions of further studies in the field is a generalization of the theory for describing magnetization curves and Mössbauer spectra of AFM and ferromagnetic nanoparticles in an applied magnetic field as well as for the presence of metamagnetism when the magnetic anisotropy energy is not much smaller than the exchange interaction, which is rather natural for very fine particles. The physical meaning of the latter case is justified from both theoretical considerations and experimental studies of finite-size effects in magnetic nanoparticles [28] whereas the physical interest is obviously due to that non-ferromagnetic nanoparticles with $k \geq 2$ in the Hamiltonian (1) are characterized by two nonequivalent pairs of local energy minima.

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