Influence of magnetocrystalline anisotropy on Mössbauer spectra in superparamagnetic phenomena

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An analysis is made of relaxation processes in Mössbauer spectroscopy of substances exhibiting superparamagnetism. The experimental results are compared with the theoretically calculated Mössbauer spectra using a stochastic model of substances with cubic magnetic anisotropy. The theory of random processes is used in the derivation of equations for calculating relaxation time and the form of the Mössbauer spectrum for an arbitrary value of the magnetic anisotropy energy.

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Mössbauer (nuclear γ resonance) spectroscopy makes it possible to investigate successfully the magnetic structure of solids. There have been many papers on this subject and, by way of example, we may refer to our own investigation[1] of such a complex ferrimagnet as hexagonal barium ferrite, for which we determined the orientations of the magnetizations of some sublattices relative to the hexagonal axis c. The Mössbauer level has a lifetime τ and a magnetic moment μ, which precesses at the Larmor frequency ω_L in a field H_{eff}. If the magnetization vector can vary with time and its characteristic time T_0 is in the range $1/\omega_L \lesssim T_0 \lesssim \tau$, we can use Mössbauer spectroscopy to study not only the magnetic structure of a given substance but also the dynamic aspects of magnetic interactions. This can be done particularly conveniently in the case of single-domain particles. Investigations of this kind not only provide information on the magnetic structure and anisotropy but also make it possible to study more deeply the nature of coercive forces and permeability of magnetic materials.

A reduction in the dimensions of single-domain particles increases the probability of thermal fluctuations of the magnetization orientations and this leads to superparamagnetic phenomena. The Mössbauer method has been used in studies of superparamagnetism of $\alpha-\text{Fe}_2\text{O}_3$, some ferrites, and other substances with various crystal and magnetic structures. Such investigations are successful only if there is a sufficiently highly developed theoretical model of relaxation processes considered as a function of the structure of matter. Up to now only one such model has been known and it can be used to obtain quite simply the form of Mössbauer spectra throughout the whole range of relaxation times of interest in superparamagnetic phenomena.[2-5] This model is based on the assumption that the part of the hyperfine interaction Hamiltonian responsible for relaxation effects may be diagonalized by selecting a certain coordinate system and corresponding wave functions, i.e., that there are only two possible directions of the magnetization vector. This situation should occur in substances with uniaxial magnetic anisotropy. The most convenient system for investigations of this kind is $\alpha-\text{Fe}_2\text{O}_3$. However, recent investigations have demonstrated anomalous behavior of this substance when particles are of the order of 80 Å.[6,7] In the case of systems with a more symmetric structure one may expect deviations from the uniaxial case. However, in analysis of the form of Mössbauer spectra it is assumed implicitly that these deviations are not of basic importance.

Our investigations of superparamagnetism in systems of simultaneously deposited hydroxides[8] demonstrated that the Dekker relaxation model cannot explain experimental results and a more general model is needed which would reduce to the Dekker treatment in the special case of a magnetic substance with uniaxial magnetic anisotropy.

1. SUPERPARAMAGNETIC PHENOMENA IN SUBSTANCES WITH CUBIC STRUCTURE

Figure 1 shows the Mössbauer spectra of amorphous (as determined by x-ray diffraction) hydroxide of trivalent iron, heated at 300 °C for 8 h, which were determined at various temperatures. Samples were prepared under conditions described in[8]. The magnetization curves indicated that the samples were in a mag-

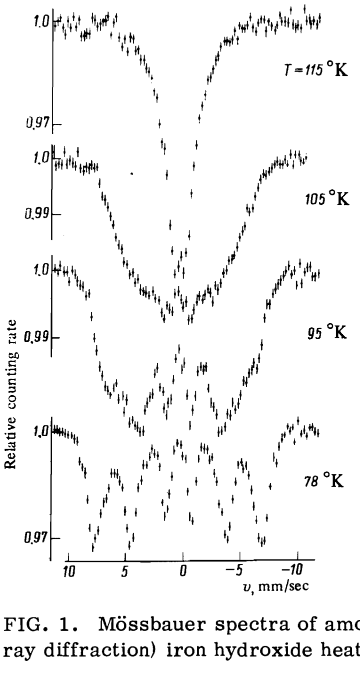

FIG. 1. Mössbauer spectra of amorphous (as deduced by x-ray diffraction) iron hydroxide heated at 300 °C for 8 h.

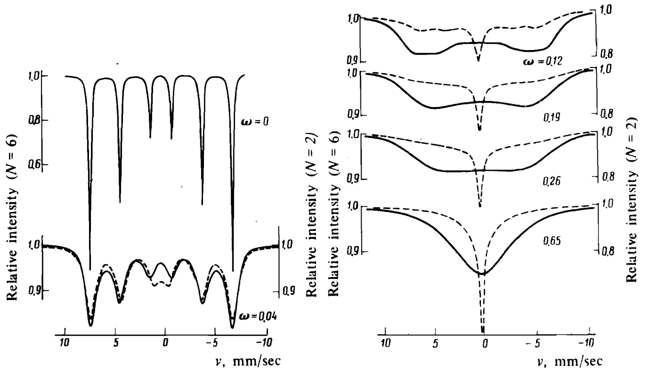

FIG. 2. Mössbauer spectra calculated using Eq. (1) for various relaxation frequencies ($N=6$). The dashed curves are the spectra calculated for the uniaxial anisotropy case ($N=2$). The values of ω are given in 10^9 sec^{-1}; N is the number of easy magnetization axes.

netically ordered state even at room temperature, although the Mössbauer spectra were in the form of a parametric doublet at 300 °K. Hence, we concluded that the material was in a finely dispersed state and it was superparamagnetic.

An interesting feature of this and similar systems[8] is the zero value (to within ± 0.01 mm/sec) of the quadrupole splitting parameter at 4.2 °K when the Mössbauer spectra can be approximated correctly by a Zeeman sextet of lines. This shows that the angle θ between the direction of the effective magnetic field and the z component of the electric field gradient (EFG) satisfies the relationship $3\cos^2\theta - 1 = 0$. This situation occurs if the effective magnetic field and the z component of the EFG tensor are oriented relative to one another in the same way as the [100] and [111] directions in a cube. Thus, the observed form of the Mössbauer spectra is governed by the cubic anisotropy of the substance and cannot be described satisfactorily by the Dekker model. The assumption of the cubic structure is not in conflict with the results of van der Giessen.[9]

It is clear from Fig. 1 that when the temperature during measurements is increased by 30–50%, the relaxation frequency increases by a factor of 10–20. This is evidence of the usual exponential dependence of the relaxation frequency on the reciprocal temperature found in superparamagnetic phenomena. There should be also a similar dependence of the relaxation frequency on the volume of the particles. Therefore, the actual distribution of the particle volumes should result in a fairly complex superposition of a large number of Mössbauer spectra corresponding to different relaxation frequencies. In the case of finely dispersed ferrites, which also have the cubic structure, such effects result in Mössbauer spectra representing superpositions of a broadened Zeeman sextet and a doublet.[10,11]

The application of general formulas for the calculation of the form of the Mössbauer spectra, obtained within the stochastic model framework,[12] meets with considerable computational difficulties because of the need for inversion of high-rank matrices. For example, in the case of easy magnetization axes of the [111] type the matrix rank for the cubic anisotropy is 64. However, in certain models of relaxation the problem can be simplified considerably.[13] We estimated the influence of the crystal structure on the form of the Mössbauer spectra and found the relaxation frequencies by calculating these spectra on the assumption that averaging over stochastic states could be made using the exact formulas of Blume.[12]

We were also acquainted with the work of Afanas'ev and Onishchenko,[14] who carried out a detailed analysis of the cubic anisotropy case and obtained an analytic expression for the form of the spectrum in the case of easy magnetization axes of the [100] type. A program which we prepared on the basis of the work of Afanas'ev and Onishchenko enabled us to estimate the average relaxation frequencies from the Mössbauer spectra by the method of least squares. However, the complexity of the observed spectra—superposition of a large number of components corresponding to different relaxation frequencies—made it difficult to select the sign of the magnetic anisotropy constant and the relationship between the probabilities of transitions per unit time between various easy magnetization axes. Therefore, we restricted our calculations to easy magnetization axes of the [100] type and assumed the probabilities of transitions per unit time to be the same between all the axes. These assumptions were not of basic importance, in contrast to the description of experimental results by the spectrum derived for the uniaxial magnetic anisotropy case, which would have been quite incorrect.

According to Afanas'ev and Onishchenko,[14] the form of the Mössbauer spectrum is given by

$$\varphi(\omega) = -\frac{1}{12\pi}\,\mathrm{Im}\,\frac{\varphi_0(\omega)}{1-{}^1/_2 ip\varphi_0(\omega)}, \tag{1}$$

where

$$\varphi_0(\omega) = \sum_{k=1}^{6} \frac{(\omega-y_k)-i(6p+\Gamma/2)}{(\omega-y_k)^2+(6p+\Gamma/2)^2}\,q_k; \tag{2}$$

here, q_k, y_k are the intensities and positions of Mössbauer lines in the case when the probability p of a transition per unit time ($\hbar=1$) between any pair of easy magnetization axes vanishes; Γ is the width of a Mössbauer level. Figure 2 shows the Mössbauer spectra calculated using Eq. (1) for various relaxation frequencies. The relaxation frequency is understood to be the probability of orientation, per unit time, along a selected easy magnetization axis, i.e., this frequency is $5p$. For comparison, Fig. 2 also shows the spectra calculated in the uniaxial anisotropy model. A simple comparison of Fig. 1 with Fig. 2 shows that the observed Mössbauer spectra cannot be approximated by the Dekker model for any reasonable assumptions. One should mention the specific, to the investigated substance, manifestation of the particle volume distribution in the Mössbauer spectra. Although the investigated substance is cubic, there is no superposition of the Zeeman sextet with broadened lines on the doublet, in contrast to finely dispersed ferrites[10,11] which can

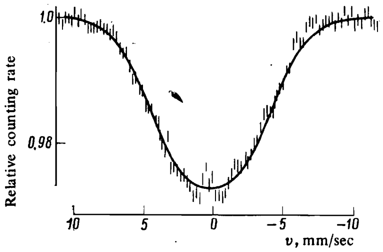

FIG. 3. Mössbauer spectrum of amorphous (as established by x-ray diffraction) hydroxide heated at 300 °C for 8 h. The continuous curve is the theoretical spectrum found by the method of least squares using the form of the spectrum given by Eq. (1); $\omega = 9\times10^8$ sec^{-1}.

be explained qualitatively by the Dekker model.

An analysis of the Mössbauer spectra shown in Fig. 1, carried out on the basis of Eq. (1), gives the most probable relaxation frequency 5×10^8 sec^{-1} at 95 °K and 7×10^8 sec^{-1} at 105 °K. The continuous curve in Fig. 3 shows the theoretical spectrum calculated by the method of least squares. The experimental Mössbauer spectra can be described satisfactorily by the theory proposed in[14].

We also attempted to approximate the distribution function of the relaxation frequencies by a Gaussian dependence. The estimates of the width of the distribution amounted to about 5% of the average value and the agreement between the theoretical and experimental spectra did not improve considerably, which indicated that the distribution was asymmetric. A better agreement between the theory and experiment should be obtained by allowing for the particle volume distribution and for the dependence of the relaxation time on the particle volume. This approach will in future give valuable information on the degree of dispersion of a system and on the dynamics of magnetization in matter. However, one must first analyze the possibility of obtaining the frequencies of transitions between various directions in a crystal as a function of its structure.

2. DESCRIPTION OF MOTION OF MAGNETIZATION VECTOR IN MATTER AND CALCULATION OF RELAXATION TIME

The problem of calculation of relaxation times includes determination of the time scale or pre-exponential factor in the expression for the relaxation time and selection of method for calculating the transition frequencies. There are several different approaches to the first task, whereas the second task involves a fairly laborious solution of the diffusion equation. Therefore, we have to consider the various methods for calculating the time scale factor and to find a simpler way for calculating the transition frequencies between various easy magnetization axes.

In Mössbauer spectroscopy it is quite correct to describe the motion of the magnetization vector in matter by classical methods. The spectroscopy of Fe^{57} allows us to investigate relaxation times in the range from 10^{-7} to 10^{-10} sec. Since the characteristic times of magnetic interactions in crystals are of the order of 10^{-13} sec, clearly, these processes are averaged over the time intervals of interest to us. This makes it possible to apply the theory of stochastic motion of the magnetization vector and to write the Hamiltonian of hyperfine interactions in the form

$$\mathscr{H}_{\mathrm{hf}}^{e,g} = A^{e,g}(I_{e,g}H(t)), \tag{3}$$

where $H(t)$ is the effective magnetic field on the nucleus, i.e., a classical and (in this case) a random quantity; $I_{e,g}$ is the spin of a nucleus in the excited and ground states; $A^{e,g}$ are the corresponding constants. The effective magnetic field follows completely the direction of magnetization in matter. The motion of the magnetization involves the motion of the momentum for which the indeterminacy of the position (in our case the angle θ) is found from the indeterminacy relationship

$$\langle s\rangle N_0 h\Delta\theta \sim h. \tag{4}$$

Here, $\langle s\rangle$ is the average (over the substance) spin of paramagnetic ions and N_0 is the number of such ions. For all reasonable particle dimensions the value of θ can be regarded as small so that the indeterminacy of the magnetization orientation can be ignored. The probability of finding a system in a particular state can be obtained from the diffusion equation ($\mathbf{x}$ are the coordinates of the magnetization vector on a sphere):

$$\frac{\partial}{\partial t}W = \sum_{i,j}\frac{1}{2}\frac{\partial^2}{\partial x_i\,\partial x_j}(W\sigma_{ij}) - \sum_i \frac{\partial}{\partial x_i}(Wa_i), \tag{5}$$

where $W(\mathbf{x}, t; \mathbf{x}_0, t_0)$ is the probability of detecting a system in a state $\mathbf{x}$ at a moment t if at a time $t = t_0$ the system is in a state $\mathbf{x}_0$; $\sigma_{ij}(\mathbf{x}, t)$ and $a_i(\mathbf{x}, t)$ are the diffusion and drift coefficients. Equation (5) applies if the equations of motion of the magnetization can be approximated by stochastic differential equations and fluctuations of the magnetization vector are due to an interaction which has the properties of white noise. It is clear that such an interaction occurs in a typical time interval of the order of 10^{-13} sec in a solid and that in the range 10^{-7}–10^{-10} sec it should be possible to obtain satisfactory results by modeling the steady-state process of white noise. Equation (5) should satisfy the steady-state distribution function

$$W_0 = z^{-1}e^{FV/kT}, \tag{6}$$

where F is the anisotropy energy density; V is the volume of a particle; k is the Boltzmann constant; T is the absolute temperature; z is the normalization factor. This distribution function gives the drift coefficients

$$a_i = e^{-FV/kT}\sum_j \frac{\partial}{\partial x_j}\left[\frac{1}{2}\sigma_{ij}e^{FV/kT}\right]. \tag{7}$$

If the stochastic equations of motion of the magnetization vector are selected in the form

$$\frac{d}{dt}x_i = E_i(\mathbf{x}, t) + \sum_j \Phi_{ij}(\mathbf{x}, t)n_j(t), \tag{8}$$

where E_i and Φ_{ij} are determined functions, and $n_j(t)$ are random processes with the properties of white noise, we find from Eq. (8) the coefficients a_i and σ_{ij}. Then, the diffusion coefficients are defined only in terms of Φ_{ij}:

$$\sigma_{ij}=c\sum_s \Phi_{is}\Phi_{js} \tag{9}$$

(c is the spectral density of white noise). If these functions depend on **x**, the drift coefficients are governed not only by the functions E_i but also (in this case) by Φ_{ij}.

Thus, in determination of the diffusion coefficients it is necessary to specify the quantities Φ_{ij}. This approach gives no assurance that all possible mechanisms of thermal fluctuations of the magnetization vector are taken into account (a similar method is used in[15]). Brown[16] assumed that the diffusion coefficients are independent of **x** and used the Gilbert equations to find the drift coefficients [by selecting suitably E_i in Eq. (8) and assuming that $\Phi_{ij}=0$] to find σ_{ij} actually from Eq. (7). However, this approach is satisfactory only to the extent that the Gilbert equations allow for thermal fluctuations of the magnetization vector in the dissipative term. One should also mention the approach suggested in[17] where general considerations are used in an attempt to estimate the time scale of thermal fluctuations in magnetic interactions.

In determining the diffusion coefficients we must find how thermal fluctuations of the spins of paramagnetic ions give rise to fluctuations of the magnetization vector. The magnetic moments of ions can be divided arbitrarily into two components: the steady component $m(T)$, which is stabilized by the exchange field, and the random component $\langle\delta m\rangle = m(0) - m(T)$. The relaxation time of the second component is h/kT. An ensemble of N_0 ions produces a fluctuating macroment of a particle $\Delta\mathbf{M}$, equal to the sum of the moments of individual ions. The thermally induced and intrinsic uncompensated magnetic moments produce a net instantaneous moment. If the relaxation time of this moment is much less than the characteristic times of the magnetic interactions, the exchange field, being isotropic, follows the direction of the net magnetic moment, i.e., the magnetization of the investigated substance relaxes. The diffusion equation for the random component of the magnetic moment of an ion $\Delta\mathbf{m}$ is of the form

$$\frac{\partial}{\partial t}W=\frac{1}{2}\frac{\langle\delta m\rangle^2}{h}kT\sum_i\frac{\partial^2 W}{\partial(\Delta m_i)^2}. \tag{10}$$

Then, the vector $\Delta\mathbf{M}$ is described similarly by

$$\frac{\partial}{\partial t}W=\frac{1}{2}N_0\frac{\langle\delta m\rangle^2}{h}kT\sum_i\frac{\partial^2 W}{\partial(\Delta M_i)^2} \tag{11}$$

and the coordinates of the magnetization vector **x** are described by

$$\frac{\partial}{\partial t}W=\frac{1}{2}\frac{\langle\delta m\rangle^2}{\langle m\rangle^2}\frac{kT}{N_0 h}\sum_i\frac{\partial^2 W}{\partial x_i^2}, \tag{12}$$

where $\langle m\rangle$ is the average uncompensated magnetic moment of a particle per paramagnetic ion. In this way we obtain the diffusion coefficient for Eq. (5):

$$\sigma_{ij}=\frac{\langle\delta m\rangle^2}{\langle m\rangle^2}\frac{kT}{N_0 h}\delta_{ij}. \tag{13}$$

According to Eq. (13), the diffusion coefficient is governed by general properties of the thermal fluctuations. However, the relaxation time of the magnetic moment depends on the specific form of the drift coefficients (7). The diffusion equation (13) is of the same form as that obtained in[18] for the determination of the relaxation time of the magnetic moment of particles in some specific cases. However, the solution method used in[18] is fairly time-consuming since it involves solution of Eq. (5). On the other hand, methods of the theory of random processes have been used to show that the average time taken to reach the boundaries $T(\mathbf{x})$ from a point **x** satisfies

$$\sum_{i,j}\frac{1}{2}\sigma_{ij}\frac{\partial^2 T(\mathbf{x})}{\partial x_i\,\partial x_j}+\sum_i a_i\frac{\partial T(\mathbf{x})}{\partial x_i}+1=0 \tag{14}$$

subject to the condition that $T(\mathbf{x})=0$ on the boundary. This equation is much simpler than Eq. (5) and in the case of a single variable, a general solution can be obtained for the uniaxial anisotropy. In the cubic anisotropy case we can vary the boundary conditions in Eq. (14) and find the times of transitions between two different pairs of easy magnetization axes as a function of their mutual orientation. In contrast, the solution method employed in[18] gives only a certain average quantity.

Thus, the results obtained allow us to obtain full information on the kinetics of magnetization which is needed for the determination of the form of Mössbauer spectra. It is interesting also to generalize the results of the stochastic theory to the case of an arbitrary relationship between FV and kT, and to analyze the possibility of simplification of the exact formulas of Blume[12] by averaging over stochastic states in the initial expressions.

3. FORM OF MÖSSBAUER SPECTRA IN STOCHASTIC RELAXATION MODEL

The determination of the form of the Mössbauer spectra in relaxation processes involves generally quantum-statistical averaging over the variables of a thermostat (crystal). In the stochastic model of relaxation this averaging is replaced with the calculation of the corresponding mathematical expectations. This can be done most simply in the case when $FV \gg kT$, i.e., when only a finite number of states of the magnetization vector, associated with a specific system of easy magnetization axes, can be realized in a system. In this case the whole kinetics of changes in the direction of the magnetization vector is described by the matrix of kinetic coefficients (probabilities of transitions per unit time between different easy magnetization axes). The methods of the thoery of random processes allow us to generalize these expressions appropriately for an arbitrary relationship between FV and kT. Moreover, we can suggest a general method of averaging over stochastic states in expressions for the form of a Mössbauer spectrum, which allows us to eliminate from the final expressions the stochastic variables for some easy magnetization axes (in the $FV \gg kT$ case).

The general expression for the form of an absorption spectrum (in the case of a thin absorber) is given by the formula

$$\varphi(\omega)=\operatorname{Re}\int_0^\infty e^{-pt}\operatorname{Tr}(\rho U^+(t)U(0))\,dt, \tag{15}$$

where $p=i\omega+\Gamma/2$, ρ is the density matrix of the investigated system (in our case a nucleus) and of the thermostat (a crystal), and $U(t)$ is the operator of the interaction of a nucleus with an electromagnetic field, corresponding to the absorption of a photon of frequency ω and wave vector k in the Heisenberg representation:

$$U(t)=e^{i\mathscr{H}t}U(0)e^{-i\mathscr{H}t}=e^{iLt}U(0). \tag{16}$$

Here, $\mathscr{H}$ is the Hamiltonian of the system and thermostat, and L is the Liouville operator whose action on any operator B is defined by

$$LB=[H, B]. \tag{17}$$

If the characteristic energy of hyperfine interactions is much less than the thermal energy, the density matrix can be divided into a product of density matrices corresponding to the investigated system and the thermostat:

$$\rho=\rho_A\rho_T. \tag{18}$$

If we introduce an operator $\mathscr{P}$, projecting the state of the system and thermostat onto the variables of the investigated system:

$$\mathscr{P}=\operatorname{Tr}(\rho_T,\ldots), \tag{19}$$

we find that Eq. (15) becomes

$$\varphi(\omega)=\operatorname{Re}\operatorname{Tr}(\rho_A U^+(0)G(p)U(0)), \tag{20}$$

where

$$G(p)=\mathscr{P}\frac{1}{p-iL}\mathscr{P}. \tag{21}$$

The expression (21) implies quantum-statistical averaging. However, if the Hamiltonian of the hyperfine interactions is represented in the form (3) the average over the thermostat states in Eq. (15), subject to Eq. (18), can be replaced with the mathematical expectation:

$$\varphi(\omega)=\operatorname{Re}\int_0^\infty e^{-pt}\operatorname{Tr}_A\left(\rho_A U^+(0)\left\langle\exp\left(i\int_0^t L_A\,dt\right)\right\rangle_{\mathbf{x}}U(0)\right). \tag{22}$$

Here, L_A is understood to be the Liouville superoperator, defined by Eq. (17), with the Hamiltonian corresponding to the sum of the Hamiltonians of the ground and excited levels of the nucleus (3). In this case the problem reduces to the calculation of

$$G=\left\langle\exp\left(i\int_0^t L_A\,dt\right)\right\rangle. \tag{23}$$

The solution can be obtained by the theory of random processes. In this case G is the solution of the following differential equation (the problem is assumed to be of the steady-state type):

$$\frac{\partial}{\partial t}G=\sum_{ij}\frac{1}{2}\sigma_{ij}\frac{\partial^2 G}{\partial x_i\,\partial x_j}+\sum_i a_i\frac{\partial G}{\partial x_i}+iL_A G \tag{24}$$

subject to the initial conditions $G(0,\mathbf{x})=1$. The solution (24) describes the function $G(t,\mathbf{x})$ introduced in accordance with Eq. (23) on condition that at $t=0$ the orientation of the effective magnetic field at the nucleus corresponds to the vector $\mathbf{x}$. In the case of Eq. (22), it is necessary to average over possible initial states in accordance with the formula

$$\left\langle\exp\left(i\int_0^t L_A\,dt\right)\right\rangle_{\mathbf{x}}=\int W_0(\mathbf{x})G(\mathbf{x},t)\,d\mathbf{x}. \tag{25}$$

Thus, Eq. (24) gives the solution of the problem in its general form, i.e., for any relationship between FV and kT. However, under experimental conditions (for $FV \gg kT$) the magnetization states are frequently realized in a finite number (N) of possible states. Then, Eq. (24) transforms to

$$\frac{d}{dt}G=MG+iL_A G, \tag{26}$$

and Eq. (25) to

$$\left\langle\exp\left(i\int_0^t L_A\,dt\right)\right\rangle_{\mathbf{x}}=\sum_{\alpha,\beta}G_{\alpha,\beta}W_0(\mathbf{x}_\beta). \tag{27}$$

The matrix M can be obtained by solving Eq. (14) with appropriate boundary conditions, i.e., by determining the transition time between various pairs of easy magnetization axes.

The solution of Eq. (27) is of the form

$$G(t)=\exp(iL_A t+Mt). \tag{28}$$

We now find the form of a Mössbauer spectrum

$$\varphi(\omega)=\operatorname{Re}\operatorname{Tr}\{U^+(0)(p-iL_A-M)^{-1}U(0)\}. \tag{29}$$

The expression (29) was obtained in[15] within the stochastic theory framework. Direct calculations based on Eq. (29) meet with considerable mathematical difficulties because it is necessary to invert high-rank matrices. However, we shall show that Eq. (28) can be simplified by averaging Eq. (26) over stochastic variables, i.e., it is possible to reduce the matrix rank from $(2I_e+1)\,(2I_g+1)N$ to $(2I_e+1)\,(2I_g+1)$.

The expression for the form of a Mössbauer spectrum of a polycrystalline sample becomes[19]

$$\varphi(\omega)=\mathrm{Re}\sum_k q_k(k,\alpha|\,(p-iL_A-M)^{-1}|j,\beta)\,W_0(x_\beta), \tag{30}$$

where $|k,\ \alpha)\equiv|m_e,\ \alpha\rangle\langle m_g,\ \alpha|$, $k\equiv(m_e,\ m_g)$ and q_k is the probability of a k-th Mössbauer transition. We shall go over from the basis $|k,\ \alpha)$ to the basis $|k(\alpha),\ \alpha)$:

$$|k(\alpha),\alpha)\equiv|m_e(\alpha),\alpha\rangle\langle m_g(\alpha),\alpha|,\quad k(\alpha)\equiv(m_e(\alpha),\ m_g(\alpha)), \tag{31}$$

where $m_e(\alpha)$ and $m_g(\alpha)$ represent the excited and ground states of a nucleus with a definite projection onto the z axis parallel to the direction α. If all the stochastic states are equiprobable, we find that

$$\begin{gathered}\varphi(\omega)=\mathrm{Re}\frac{1}{N}\sum_{k,j}\sum_{\alpha,\beta} q_k(k(\alpha),\alpha|G(p)|j(\beta),\beta)\,(j(\beta)|k(\alpha)),\\ (k(\alpha),\ \alpha|M|j(\beta),\ \beta)=(k(\alpha)\,|j(\beta))M_{\alpha,\beta},\\ (k(\alpha),\ \alpha|L_A|j(\beta),\ \beta)=\omega_k\delta_{kj}\delta_{\alpha,\beta},\end{gathered} \tag{32}$$

where ω_k is the frequency of a k-th Mössbauer transition in the case when $M=0$.

We shall analyze the case when averaging over stochastic indices can be carried out in Eq. (26) term by term. We shall separate formally the stochastic indices in the matrices M and G and we shall find when the following relationship applies:

$$\mathcal{SP}(MG)\equiv\sum_{\alpha,\beta,\gamma}M_{\alpha\gamma}G_{\gamma\beta}=\frac{1}{N}\mathcal{SP}(M)\,\mathcal{SP}(G). \tag{33}$$

This is possible if the matrix M can be expanded as a system of matrices e_s, all of whose elements vanish, except N terms which are equal to unity. Then, each column and row does not contain more than one unity. A set of these matrices is closed in respect of multiplication so that we have the following obvious equality

$$\mathcal{SP}(e_se_r)=\frac{1}{N}\mathcal{SP}(e_s)\,\mathcal{SP}(e_r). \tag{34}$$

Multiplication of e_s by any matrix G results in a transposition of rows G_s, so that

$$\mathcal{SP}(e_sG)=\mathcal{SP}(G)=\frac{1}{N}\mathcal{SP}(e_s)\,\mathcal{SP}(G). \tag{35}$$

If, for a given system of easy magnetization axes, the set of rotations resulting in coincidence of a system of coordinates of any one of them with all others (the z axis is directed along an easy magnetization axis) forms a group, there are N different rotation operators between the various pairs of axes. The matrix of these operators for a system of easy magnetization axis gives, by its coincidence terms, the required expansion of the matrix M in Eq. (32). It follows from symmetry of these pairs of axes that the elements of the matrix M are all the same. Then, Eq. (26) becomes

$$d\tilde{G}/dt=\tilde{M}\tilde{G}+i\tilde{L}_A\tilde{G}, \tag{36}$$

so that

$$\varphi(\omega)=\mathrm{Re}\frac{1}{N}\sum_{k,j}q_k(k|\tilde{G}(p)|j)\,(j|D|k), \tag{37}$$

where

$$\begin{gathered}(k|\tilde{M}|j)=\frac{1}{N}\sum_{\alpha,\beta}(k(\alpha)\,|j(\beta))\,M_{\alpha\beta},\\ (k|\tilde{L}_A|j)=\omega_k\delta_{kj},\quad (j|D|k)=\frac{1}{N}\sum_{\alpha,\beta}(j(\alpha)\,|k(\beta)).\end{gathered}$$

Thus, we have been able to reduce by a factor of N the rank of the matrix G. However, in special cases the problem can be simplified still further, as demonstrated in[14] when an analytic expression can be obtained by applying the symmetry of the problem to easy magnetization axes of the [100] type.

We shall simplify the estimates in Eq. (37) by replacing $(k(\alpha)|\,j(\beta))$ with $|\,(k(\alpha)|\,j(\beta)|^2$. If we compare the results obtained in this way with the exact results calculated in accordance with[14], we find that the differences are slight and they amount to about 5%.

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