PHYSICAL REVIEW B VOLUME 62, NUMBER 5 1 AUGUST 2000-I

Spin-lattice-relaxation-like model for superparamagnetic particles under an external magnetic field

H.-D. Pfannes, A. Mijovilovich, R. Magalhães-Paniago, and R. Paniago
Departamento de Física, Universidade Federal de Minas Gerais, CP 702, 30123-970 Belo Horizonte, Brazil

(Received 22 November 1999)

Small monodomain magnetic particles of uniaxial magnetic anisotropy are considered. The superparamagnetic relaxation is assumed to happen by coherent rotation of the spins. The results of existing models for the calculation of superparamagnetic relaxation times are shortly reviewed. A different model based on phonon interaction with the total spin of the particle under the presence of an external magnetic field is presented and corresponding relaxation times are calculated and compared with the existing theories. The calculation of Mössbauer superparamagnetic relaxation spectra in the low-temperature limit and for higher temperatures is discussed.

I. INTRODUCTION

Ultrafine single domain magnetic particles are often found in soils, rocks, and living organisms or in artificially manufactured materials. They are of great interest in fundamental science and technology because of their nanometric size and magnetic properties that differ from the corresponding bulk materials. Many studies, like, e.g., of catalysts, high-density recording media, ferrofluids, argiles, ceramics, paintings, magnetic bacteria, ferritin, and others, in which nanosized magnetic particles are important, have been reported in the literature.

The magnetization at low temperatures in such particles is oriented near easy magnetization directions which correspond to minima of the magnetic anisotropy energy, separated by energy barriers of certain heights. An external field changes the relative depths of the minima. As the temperature increases, the magnetization can overcome this barrier and turn over to near another easy direction with a certain magnetization reversal rate τ^{-1}. The particle is said to exhibit a superparamagnetic behavior if the characteristic time of measurement (time window) of the method used for the determination of the magnetization is greater than τ. Among various methods, Mössbauer spectroscopy has been widely used for the investigation of iron-containing superparamagnets since its characteristic time of approximately 10^{-8} s lies in the range of superparamagnetic relaxation times at 100–300 K of many species of magnetic nanosized particles.

The overturn of the magnetization to a different orientation happens by rotation of the spins. In the rest of the paper we consider only the case of ''coherent rotation,'' i.e., all spins remain in the initial mutual (parallel) configuration throughout the rotation.[1] This mode minimizes the exchange interaction and is prevalent for sufficiently small particles. For bigger particles, where the anisotropy energy is minimized, other modes (''buckling'' or ''curling'') are possible (see, e.g., Ref. 1).

For simplicity, we presume the existence of uniaxial anisotropy, no size dispersion (all particles have the same size and shape), and no interparticle interaction. We assume also that the orientation of the easy direction of all particles is along the z direction, i.e., when the anisotropy is due, e.g., to uniaxial form anisotropy, all particles are equally oriented in space. With these assumptions and under the presence of an external field with induction B applied along the $+z$ direction, the anisotropy energy E is given by[1–4]

$$E(\Theta)=KV\sin^2(\Theta)-M_SVB\cos(\Theta), \tag{1.1}$$

where K is the anisotropy constant, V the volume, M_S the (saturation) magnetization per volume of the particles, and Θ represents the angle between the magnetization and the $+z$ direction. $E(\Theta)$ exhibits one minimum at $\Theta=0$ (magnetization parallel to the external field) with energy $E(0)=-M_SVB$ and another at $\Theta=\pi$, with higher energy $E(\pi)=+M_SVB$ (magnetization antiparallel to the external field). Above a limit field $B_{lim}=2K/M_S$ only one minimum exists. For $B=0$ both minima are separated by an energy barrier of height $E(\pi/2)=KV$. The probability $f(\Theta)d\Theta$ to find the magnetization oriented towards Θ is given by the thermal average $f(\Theta)=g(\Theta)/\int_0^\pi g(\Theta)d\Theta$ with $g(\Theta)=\exp[-E(\Theta)/(k_BT)]\sin\Theta$.[1,2] For high temperature and low fields this is different from zero in the whole range $0\leqslant\Theta\leqslant\pi$, meaning that the magnetization can fluctuate between different directions. It is our objective to attribute relaxation rates to these fluctuations of the magnetization direction and to derive explicit expressions for them.

II. CLASSICAL MODELS

The classical theories of superparamagnetism are the models of Néel[4] and Brown.[5] In both models coherent rotation of the spins is assumed.

Néel notes that at low temperature and in the presence of an external field directed along the $+z$ direction, the magnetization of P particles of a total of N identical particles present, at an instant t, is found near the $+z$ direction and that of the remaining $(N-P)$ particles near the $-z$ direction. Corresponding time constants τ_+ and τ_- are introduced by writing the balance equation

$$\dot{P}=-P/\tau_+ +(N-P)/\tau_- , \tag{2.1}$$

where τ_+ and τ_- correspond to the passage of magnetizations from $\Theta=0$ [lower minimum of $E(\Theta)$] to $\Theta=\pi$ [higher minimum of $E(\Theta)$] or vice versa, respectively. With the solution of Eq. (2.1) the total relative magnetization $M(t)$, which is proportional to $P-(N-P)=2P-N$, can be written as

$$M(t)/M_S=N(\tau_+-\tau_-)/(\tau_++\tau_-)$$
$$+2[P(0)-N\tau_+/(\tau_++\tau_-)]\exp(-t/\tau) \tag{2.2}$$

with $\tau^{-1}=\tau_+^{-1}+\tau_-^{-1}$.

For the calculation of $\tau_\pm$ Néel relates the vibrational strain energy of the particles to the thermal energy, calculates the corresponding magnetostrictive energy, and from this the magnetic anisotropy field in which the magnetization precesses. The superparamagnetic relaxation rates $\tau_\pm^{-1}$ are then calculated by multiplying the precession rates by the population of the states near the top of the barrier and by an Arrhenius factor.[4,6] Including also demagnetization effects Néel obtains $[\alpha\equiv\beta KV=KV/(k_BT)]$

$$\tau_{\pm Neel}^{-1}=(2K/\pi\mathrm{G})^{1/2}\gamma_0M_S^{-1}|3G\mu+DM_S^2|\alpha^{1/2}(1-h^2)^{1/2}$$
$$\times(1\pm h)\exp[-\alpha(1\pm h)^2], \tag{2.3}$$

where γ_0 is the gyromagnetic ratio ($\gamma_0=\mathrm{g}\mu_B/\hbar\approx ge/m$, $\mu_B=$Bohr magneton $\approx 9.27\times10^{-24}$ J/T, $g=$electronic g factor, e/m specific charge of the electron), G is Young's modulus, μ is the longitudinal magnetostriction constant, D the demagnetization factor, and h is the reduced field $h=M_SB/2K$.

Brown[5] considers a random walk of the magnetization direction similar to normal Brownian motion. From Gilbert's equation for the movement of the magnetization, in which a dissipative term $\eta d\vec{M}/dt$ and a random-field term $d\vec{h}(t)/dt$ is included, a Fokker-Planck-type equation is derived, whose solution can be written as a series containing exponentially decaying time-dependent terms. The corresponding decay rate constants are the eigenvalues of the Fokker-Planck equation. In the case of uniaxial symmetry the smallest positive eigenvalue λ, which determines the dominant (longest) relaxation time constant τ, can then be calculated from the solution of the following differential equation:

$$\frac{d}{dt}\left((1-x^2)\frac{d\Phi(x)}{dx}\exp[-E(\Theta)/(k_BT)]\right)$$
$$+\lambda\Phi(x)\exp[-E(\Theta)/(k_BT)]=0 \tag{2.4}$$

with $\lambda=2\alpha M_S/(\tau\gamma_0K)$, where for the dissipation constant $\eta=(\gamma_0M_S)^{-1}$ is assumed. From this equation Brown deduces assymptotic values of the relaxation rate for high ($\alpha\ll1$) and low ($\alpha\gg1$) temperature:

$$\alpha\ll1{:}\,\tau_{Br}^{-1}\approx(\gamma_0K/M_S)\alpha^{-1}[1-(2/5)\alpha+(48/875)\alpha^2$$
$$+(2/5)h^2\alpha^2] \tag{2.5}$$

and

$$\alpha\gg1{:}\,\tau_{\pm Br}^{-1}\approx(\gamma_0K/\pi^{1/2}M_S)\alpha^{1/2}(1-h^2)(1\pm h)$$
$$\times\exp[-\alpha(1\pm h)^2]. \tag{2.6}$$

Bessais, Ben Jaffel, and Dormann[7] solved the Fokker-Planck equation by introducing Fourier and Chebyshev series and derived an analytical expression for the smallest positive eigenvalue. An external field was not included in their calculations. By comparing with numerical solutions an agreement within 1% in the range $0.5\leqslant\alpha\leqslant50$ was established. The corresponding relaxation rate, assuming again $\eta=(\gamma_0M_S)^{-1}$, is

$$\tau_{BBD}^{-1}=\tau_{0BBD}^{-1}\exp(-\alpha) \tag{2.7}$$

with

$$\tau_{0BBD}^{-1}=K\gamma_0M_S(1+\alpha/4)^{5/2}\alpha^{-1}. \tag{2.8}$$

In the limit of high temperature τ_{0BBD} approaches zero as does τ_{Brown} from Eq. (2.5).

A different approach to superparamagnetic relaxation, especially adapted to the calculation of Mössbauer spectra of superparamagnetic particles, has been proposed by Jones and Srivastava (''many states'' model[8]). With this model also ''collective excitations''[1] can be taken into account in a correct way. The Mössbauer spectrum (diagonal hyperfine interaction) $I(\omega)$ for a pair of lines, (e.g., lines 1 and 6) of a six-line spectrum with splitting proportional to the z component of the magnetization is

$$I(\omega)\propto-2\,\mathrm{Re}(\vec{W}\mathbf{M}^{-1}\vec{\mathbf{1}}) \tag{2.9}$$

with the matrix

$$\mathbf{M}=[i(\omega-\omega_i)+\Gamma]\mathbf{1}-\mathbf{R}, \tag{2.10}$$

where the row vector $\vec{W}$ consists of probabilities (Boltzmann factors) of the different magnetization directions (attributing ''states'' S_z to them), the diagonal matrix $[i(\omega-\omega_i)+\Gamma]\mathbf{1}$ contains the line positions ω_i according to the hyperfine splitting, Γ is the natural linewidth of the Mössbauer isotope, and $\vec{\mathbf{1}}$ is a column vector with all elements equal to 1. $\mathbf{R}$ is a relaxation matrix whose off-diagonal elements r_{ij} are the transition probabilities per time w_j^i between the states i and j $(i\neq j)$ and whose diagonal elements are $r_{ii}=-\Sigma_jw_i^j(i\neq j)$. The complete Mössbauer spectrum is obtained by summing up the separately calculated three two-line spectra from Eq. (2.9), weighted with the adequate intensity factors, in our case, e.g., 3:0:1 when the γ direction is parallel to the z direction. A more exact expression, valid when off-diagonal hyperfine interactions are present, implies in the use of superoperators like in Ref. 9.

Jones and Srivastava[8] assume that random fields give rise to transitions between adjacent states, i.e., only matrix elements $\langle S_z+1|S_+|S_z\rangle$ and $\langle \mathrm{S}_z|\mathrm{S}_-|\mathrm{S}_z+1\rangle$are different from zero and hence the matrix is tridiagonal. It is shown that in the continuum limit the Mössbauer line shape can be obtained from the numerical solution of a differential equation. In the low-temperature regime and in the presence of an external field they derive a relaxation rate $\tau_{\pm JS}^{-1}$,[8]

$$\tau_{\pm JS}^{-1}=A\pi^{1/2}\alpha^{3/2}(1-h^2)(1\pm h)\exp[-\alpha(1\pm h)^2], \tag{2.11}$$

where A is a parameter proportional to the square of the random field and could depend on K,M_S,T, etc. In a later publication[6] Jones and Srivastava questioned whether classical fluctuations could be responsible for superparamagnetic relaxation since their correlation times, which are supposed to be of the order of 10^{-13} s are shorter than the precession time of $\geqslant 10^{-12}$ s that is needed for a magnetization oriented at $\Theta \approx 85$ degrees to turn to the other side of the barrier. In our model presented below the superparamagnetic relaxation is supposed to be due to interaction of the spins with long-wavelength (low-frequency) phonons and therefore no correlation problem arises.

For the case of magnetic molecules with a net spin of $S = 10$ Villain *et al.*[10] calculated a spin-relaxation rate (without external field) based on normal spin-phonon paramagnetic relaxation theory and a Debye model. In the low-temperature limit the rate τ_V^{-1} [approximated from Eq. (2.11) of Ref. 10] is

$$\tau_V^{-1} \approx 3|B_1^0|^2(KV)^3(2\pi\hbar^4\rho v^5\alpha S^4)^{-1}\exp(-\alpha), \tag{2.12}$$

where ρ and v is the density and sound velocity, respectively, of the particle and B_1^0 is a spin-phonon interaction constant.

It is our main intention in the following to work out expressions comparable to Eqs. (2.3)–(2.7), (2.11), and (2.12) based on a spin-phonon-interaction-like relaxation model. In contrast to Ref. 10 we include an external field in the calculations, take electronic matrix elements into account, and allow for higher-order terms in the spin-phonon coupling Hamiltonian. Finally we discuss the calculation of Mössbauer spectra of superparamagnetic samples.

III. MODEL

With the simplified assumptions already made above (uniaxial anisotropy, coherent rotation, no interparticle interaction) we adopt now the picture for superparamagnetic relaxation described in the following (see also Ref. 3).

The magnetization of the equally sized (monodispersed) particles is considered as arising from a large spin S whose direction relative to the anisotropy axis fluctuates due to interaction with phonons. In order to reach the opposite easy direction $-z$ the spin S must pass through intermediate levels.

By analogy with the classical anisotropy energy (1.1),

$$\begin{aligned} E &= KV - KV\cos^2\theta - M_S VB\cos\theta \\ &= KV - A(S\cos\theta)^2 - g\mu_B B(S\cos\theta), \end{aligned} \tag{3.1}$$

we write, up to a constant, a spin-Hamiltonian H_{sp} for the (anisotropy) energy of S in a field B,

$$H_{sp} = -AS_z^2 - 2h'S_z, \tag{3.2}$$

where $KV = AS^2$ (height of energy barrier without external field), $M_S V = g\mu_B S$, and $2h' = g\mu_B B$ (B along the $+z$ direction). Energy eigenvectors of H_{sp} are $|S_z\rangle = |m\rangle$ and eigenvalues are

$$E_m = -Am^2 - 2h'm \tag{3.3}$$

with $m = -S, -S+1, \ldots, -h'A$ (top of barrier), ... $S-1, S$, where we have assumed that h'/A is a positive integer. The function E_m vs m is shown in Fig. 1. It exhibits a maximum at $m = -h'/A$ with $E_m(-h'/A) = h'^2/A$. There are two energy minima up to a limit field $h'_{lim} = AS$ whereas for higher fields only one minimum exists. Without external field ($h' = 0$) the barrier height is $E_B = AS^2$ and for $h' > 0$ it can be written as

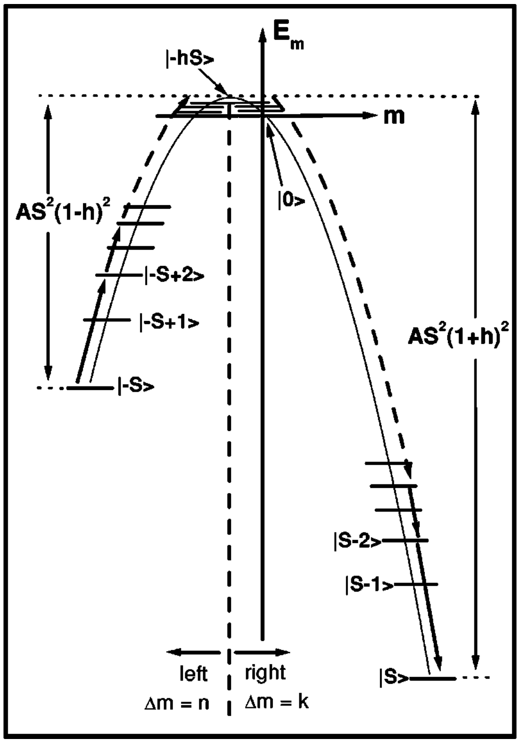

FIG. 1. Anisotropy energy E_m vs eigenvalues m under an external field with $B = 2hAS/g\mu_B$ (see text). The arrows indicate an example of transition $|-S\rangle \rightarrow |S\rangle$ via phonon anihilation (left) and creation (right) with $\Delta m = n = k = 2$.

$$E_B^{\pm} = AS^2(1 \pm h)^2, \tag{3.4}$$

where $0 \leqslant h \equiv h'/h'_{lim} \leqslant 1$ and the positive (negative) sign refers to whether m is on the right (left)-hand side of the maximum in Fig. 1 ($m \geqslant -hS$ or $m \leqslant -hS$, respectively).

We calculate successive energy differences $E_m - E_{m+k}$ or $E_m - E_{m-n}$ that differ by $\Delta m = k$ or n on the right- or left-hand side of the maximum in Fig. 1, respectively,

$$E_m - E_{m+k} = Ak^2(1+2q) \tag{3.5a}$$

with $m = -hS + kq,\ q = 0,1,\ldots,S(1+h)/k - 1$, and

$$E_m - E_{m-n} = An^2(1+2q) \tag{3.5b}$$

with $m = -hS - nq,\ q = 0,1,\ldots,S(1-h)/n - 1$, where both m and q are counted from top to bottom of the barrier potential. In order to obtain an expression for the transition probabilities between different spin levels of H_{sp} we write the Hamiltonian of the spin-phonon system as

$$H = H_{sp} + H_{ph} + H_{sp-ph}, \tag{3.6}$$

where the eigenstates of the phonon operator H_{ph} are the usual phonon states, characterized by phonon occupation numbers n_j. The spin-phonon interaction H_{sp-ph} induces transitions in the spin and phonon subsystems and may be described by a dynamic spin-Hamiltonian[9,11,12]

TABLE I. ''Standard'' values used in numerical calculations. B_l^p is measured in energy units cm^{-1}.

Diameter $d=9\times10^{-9}$ m$=90$ Å	Volume $V=\pi d^3/6=3.82\times10^{-25}$ m^3
Anisotropy constant $K=7\times10^4$ Jm^{-3}	Anisotropy energy $KV=AS^2=2.67\times10^{-20}$ J
Density $\rho=5000$ kgm^{-3}	Sound velocity $v=3000$ ms^{-1}
Lattice constant $a=8.4\times10^{-10}$ m$=8.4$ Å	Spin $S=3222$ (five spins per a^3)
$C\equiv3(B_l^p)^2/\pi\hbar^4\rho v^5=1.26\times10^{69}$ $(B_l^p/\mathrm{cm}^{-1})^2$ J^{-3} s^{-1}	$C'=C(AS^2)^3=2.4\times10^{10}(B_l^p/\mathrm{cm}^{-1})^2$ s^{-1}
$\lambda_{min}=2a=16.8$ Å	$\lambda_{max}=d=90$ Å
$E_{phmax}=2\pi\hbar v/\lambda_{min}=1.18\times10^{-21}$ J	$E_{phmin}=2\pi\hbar v/\lambda_{max}=2.21\times10^{-22}$ J

$$H_{sp-ph}=\sum_{l,p} B_l^p O_l^p(\varepsilon_{\alpha\nu}+\varepsilon_{\alpha\nu}^2+\cdots), \tag{3.7}$$

where ε_{av} is an angle-averaged lattice strain operator given by ($M=$crystal mass, ω_j and $\vec{k}_j=$frequency and wave vector of phonon mode j)

$$\varepsilon_{\alpha\nu}=\sum_j \left(\frac{\hbar}{2M\omega_j}\right)^{1/2} k_j[a_j^+\exp(-i\vec{k}\vec{r}_j)+a_j\exp(i\vec{k}\vec{r}_j)]. \tag{3.8}$$

O_l^p are dynamical crystal-field operators of order l in the spin variables and B_l^p the corresponding coupling constants to the phonons.[11,12] For the present we do not restrict the order of the O_l^p since the superparamagnetic spin-strain interaction may be described by higher order than $l=1$[8] or $l=2$[10]. The phonon creation and annihilation operators a_j^+ and a_j act on the combined spin-phonon states $|m,j\rangle=|m\rangle|\cdots n_j\cdots\rangle$ leading to phonon matrix elements $\langle\cdots n_j+1\cdots|a_j^+|\cdots n_j\cdots\rangle=(n_j+1)^{1/2}$ and $\langle\cdots n_j-1\cdots|a_j|\cdots n_j\cdots\rangle=n_j^{1/2}$ with the thermal average $n_j=\langle n_j\rangle=\{\exp[h\omega_j/(k_BT)]-1\}^{-1}$ (Bose-Einstein factor). The transition rate $w_m^{m'}\equiv w(|m,j\rangle\rightarrow|m',j'\rangle)$ of a transition $|m,j\rangle\rightarrow|m',j'\rangle$ induced by H_{sp-ph} can then be calculated by the golden rule

$$w_m^{m'}=(2\pi/\hbar)|\langle m',j'|H_{sp-ph}|m,j\rangle|^2\delta(E_{m'}-E_m\pm\hbar\omega_j), \tag{3.9}$$

where the δ function accounts for energy conservation, the ''$-$'' sign is valid for $E_{m'}>E_m$ (phonon annihilation) and the ''$+$'' sign for $E_m>E_{m'}$ (phonon creation). In calculating the matrix elements $w_{m'}^m$, in principle, one has to invert the sign of the magnetic field,[13] but also the sign of the spin numbers has to be inverted, so that H_{sp-ph} remains unaltered. Introducing Eqs. (3.8) in (3.9), restricting ε_{av} to first order (one-phonon process) and taking for simplicity only one term (l,p) in the electronic matrix element into account, results for phonon annihilation in

$$w_m^{m'}=\frac{\pi}{M}(B_l^p)^2|\langle m'|O_l^p|m\rangle|^2\sum_j \frac{k_j^2}{\omega_j}\frac{\delta(E_{m'}-E_m-\hbar\omega_j)}{\exp(\hbar\omega_j/k_BT)-1}. \tag{3.10}$$

We introduce the Debye model in the long-wavelength limit (acoustic branch with dispersion relation $\omega=vq$, $v=$weighted average of transverse and longitudinal sound velocities) by replacing the sum by an integration $\int_0^{\omega_D}g(\omega)d\omega$, where $g(\omega)$ is the Debye distribution function $g(\omega)=(3V/2\pi^2v^3)\omega^2$ and $\omega_D=(6\pi^2/V)^{1/3}v$, and obtain (density $\rho=M/V$)

$$w_m^{m'}=\frac{3(B_l^p)^2|\langle m'|O_l^p|m\rangle|^2}{2\pi\hbar^4\rho v^5}\frac{(E_{m'}-E_m)^3}{\exp[(E_{m'}-E_m)/(k_BT)]-1}, \tag{3.11}$$

where $E_{m'}>E_m$ for phonon annihilation and $E_m>E_{m'}$ for phonon creation.

For the ratio of up and down transitions follows $w_m^{m'}/w_{m'}^m=\exp[-(E_{m'}-E_m)/(k_BT)]$ in accordance with a Boltzmann population of the levels.

It may be interesting to observe that in the framework of the Debye model the transition probability for small spin-energy differences tends to zero and not to infinity as one would take for granted intuitively. The reason of this is the cubic dependence on energy in the transition probabilities which stems from the depletion of low-energy phonons $[g(\omega)\propto\omega^2]$ in the Debye model. For small isolated particles however the minimum one-phonon energy is of the order of $2\pi\hbar v/\lambda$. This could be greater than the energy differences (3.5) for low k or n values, so that no energy conserving spin-transition could occur. Nevertheless, for the following we presume the presence of sufficient low-energy phonons which stem, e.g., from the matrix in what the superparamagnetic particles are embedded.

In order to extract later on concrete values for relaxation times from the theoretical expressions developed below we fix the numerical values related to the superparamagnetic particle listed in Table I. These values correspond to the values used in Ref. 14 for a ferrofluid (powder), but are also typical for other superparamagnetic particles.

IV. THREE-LEVEL SYSTEM

With the intention of delineating the basic ideas for calculating relaxation times we start with a simple three-level system where p_S, p_{-hS}, and p_{-S} are the fractional populations of the corresponding levels. We have then, by detailed balance, the rate equations

$$\dot{p}_S=w_{-hS}^S p_{-hS}-w_S^{-hS}p_S, \tag{4.1a}$$

$$\dot{p}_{-S}=w_{-hS}^{-S}p_{-hS}-w_{-S}^{-hS}p_{-S}, \tag{4.1b}$$

$$\dot{p}_{-hS}=w_{-S}^{-hS}p_{-S}+w_S^{-hS}p_S-(w_{-hS}^S+w_{-hS}^{-S})p_{-hS} \tag{4.1c}$$

and the condition

$$p_S+p_{-hS}+p_{-S}=1. \tag{4.2}$$

With Eqs. (4.2) and (4.1b) one can eliminate p_{-hS} from the first equation and obtains a second-order linear differential equation for p_S

$$\begin{aligned}\ddot{p}_S+\dot{p}_S\{[1+\exp(-\alpha_+)]w^S_{-hS}+[1+\exp(-\alpha_-)]w^{-S}_{-hS}\}\\ +p_S w^S_{-hS}w^{-S}_{-hS}\{[1+\exp(-\alpha_+)]\\ \times[1+\exp(-\alpha_-)]-1\}\\ =w^S_{-hS}w^{-S}_{-hS}\exp(\alpha_-),\end{aligned} \tag{4.3}$$

where $\alpha_\pm=E_B^\pm/k_BT$. The solution is

$$\begin{aligned}p_S=c_{1S}\exp(-\lambda_1 t)+c_{2S}\exp(-\lambda 2t)+\exp(-\alpha_-)\\ \times\{[1+\exp(-\alpha_+)][1+\exp(-\alpha_-)]-1\}^{-1},\end{aligned} \tag{4.4}$$

where the constants c_{1S} and c_{2S} depend on the initial conditions, and the two characterisitic frequencies are

$$\tau_{1,2}^{-1}=\lambda_{1,2}=(A^++A^-)/2\pm[w^S_{-hS}w^{-S}_{-hS}+(A^+-A^-)^2/4]^{1/2} \tag{4.5}$$

with $A^\pm=[1+\exp(-\alpha_\pm)]w^{\pm S}_{-hS}$. For p_{-S} one deduces an identic homogeneous equation and thus the same characteristic frequencies $\tau_{1,2}^{-1}$. The rate Eqs. (4.1) and consequently $\tau_{1,2}^{-1}$ are invariant under a simultaneous change of $(S,h)\rightarrow(-S,-h)$. It is not possible from Eq. (4.1) to define relaxation times like τ_+ and τ_- and also not a single relaxation time unless one characteristic time $\tau_{1,2}$ in Eqs. (4.5) and (4.4) is predominant. In general, the return of p_S and p_{-S} to equilibrium after release of a transient is determined by both times τ_1 and τ_2.

Another possibility to define relaxation times, in the case of small perturbations, is to focus on a pair of levels, in our case especially $|S\rangle$ and $|-S\rangle$, under the assumption that the occupation of all other levels remains constant (stationarity condition). In this case, in fact, we deal with a pseudo-two-state relaxation system. Then $\dot{p}_{-hS}=0$ in Eq. (4.1c) and from this we obtain[10]

$$\begin{aligned}J&\equiv-\dot{p}_S\\ &=w_S^{-hS}p_S-w^S_{-hS}p_{-hS}\\ &=w^{-S}_{-hS}p_{-hS}-w_{-S}^{-hS}p_{-S}\\ &=\dot{p}_{-S}\end{aligned} \tag{4.6}$$

and can therefore express p_S by p_{-S},

$$p_S=J\Lambda+\Gamma p_{-S}, \tag{4.7}$$

with

$$\Lambda=(w_S^{-hS})^{-1}+(w^S_{-hS}/w_S^{-hS})(w^{-S}_{-hS})^{-1} \tag{4.8}$$

and

$$\Gamma=(w^S_{-hS}/w_S^{-hS})(w_{-S}^{-hS}/w^{-S}_{-hS})=\exp(\alpha_+)\exp(\alpha_-). \tag{4.9}$$

We have therefore $J=(p_S-\Gamma p_{-S})/\Lambda$ and the equations

$$\dot{p}_S-\dot{p}_{-S}=-2J=-(2/\Lambda)(p_S-\Gamma p_{-S}) \tag{4.10a}$$

and

$$\dot{p}_S-\Gamma\dot{p}_{-S}=-J-\Gamma.J=[(1+\Gamma)/2](\dot{p}_S-\dot{p}_{-S}) \tag{4.10b}$$

which results, up to a constant, in $p_S-\Gamma p_{-S}=[(1+\Gamma)/2](p_S-p_{-S})$ and $\dot{p}_S-\dot{p}_{-S}=(-2/\Lambda)[(1+\Gamma)/2](p_S-p_{-S})$. Thus we obtain a relaxation rate

$$\tau^{-1}=(1+\Gamma)/\Lambda. \tag{4.11}$$

Since $\dot{p}_{-hS}=0$ we can regard p_S and p_{-S} as belonging to a two-level system and obtain, in analogy with Eq. (2.1) from Eqs. (4.6) and (4.9) $\dot{p}_S=p_{-S}/\tau_--p_S/\tau_+=-J=-p_S/\Lambda+\Gamma p_{-S}/\Lambda$ and thus

$$\tau_+=\Lambda,\quad \tau_-=\Lambda/\Gamma\ \text{ and } \tau^{-1}=\tau_+^{-1}+\tau_-^{-1} \tag{4.12}$$

with τ^{-1} in accordance with Eq. (4.11). For the three-level system, suppressing the electronic matrix elements, the result is thus

$$\begin{aligned}\tau_\pm^{-1}=CE^3_{B+}E^3_{B-}\\ \times\frac{\exp(-\alpha_\pm)}{E^3_{B-}[1-\exp(-\alpha_+)]+E^3_{B+}[1-\exp(-\alpha_-)]}.\end{aligned} \tag{4.13}$$

For $h=0$

$$\tau^{-1}=\frac{C'}{2}\,\frac{\exp(-\alpha)}{1-\exp(-\alpha)}, \tag{4.14}$$

where $\alpha=E_B/(k_BT)=AS^2/(k_BT)$ and $C'=C(AS^2)^3$ (cf. Table I). An equivalent formula has been given in Ref. 14. In the limit of high temperature ($\alpha\rightarrow 0$), τ^{-1} from Eq. (4.14) tends to infinity, which intuitively is physically suggestive. Assuming $B_l^p=10$ cm^{-1} the pre-exponential factor $C'/2$ in Eq. (4.14) is approximately 10^{12} s^{-1} which is within the correct order of magnitude. However, as we will see below, respecting the suppressed electronic matrix elements leads to completely unrealistically fast relaxation rates. We must therefore consider the multilevel system according to the ''real spin'' S.

V. MULTILEVEL SYSTEM

In general, instead of three levels a multilevel system with $2S+1$ levels is present (6445 levels in our example). We calculate now the relaxation times $\tau_\pm$ under the stationarity conditions $\dot{p}_i=0, i\neq S,-S$. For simplicity we only consider spin transitions with constant quantum number differences Δm (variable energy differences), where $\Delta m=k$ on the right-hand side in Fig. 1 and $\Delta m=n$ on the left-hand side. The corresponding energy differences are given by Eq. (3.5). In analogy to Eq. (4.1) the master equations in the different regions of m in Fig. 1 read: at the right-hand side in Fig. 1,

$$\dot{p}_S=w^{-S}_{S-k}p_{S-k}-w_S^{S-k}p_S \tag{5.1a}$$

with stationarity condition $\dot{p}_m=0\Rightarrow$

$$w_m^{m-k}p_m - w_{m-k}^{m}p_{m-k} = w_{m+k}^{m}p_{m+k} - w_m^{m+k}p_m \equiv J_k\,, \tag{5.1b}$$

$$m = S-k, S-2k, \ldots, -hS+k; \tag{5.1c}$$

at the top of barrier $0=\dot{p}_{-hS}\Rightarrow$

$$\begin{aligned} &w_{-hS+k}^{-hS}p_{-hS+k} - w_{-hS}^{-hS+k}p_{-hS} \\ &\quad = w_{-hS}^{-hS-n}p_{-hS} - w_{-hS-n}^{-hS}p_{-hS-n} \equiv J_{-hS}\,; \end{aligned} \tag{5.2}$$

at the left-hand side in Fig. 1,

$$\dot{p}_{-S} = w_{-S+n}^{-S}p_{-S+n} - w_{-S}^{-S+n}p_{-S} \tag{5.3a}$$

with stationarity condition $\dot{p}_m = 0 \Rightarrow$

$$\begin{aligned} w_m^{m-n}p_m - w_{m-n}^{m}p_{m-n} = w_{m+n}^{m}p_{m+n} - w_m^{m+n}p_m \equiv J_n m = -hS \\ -n, \ldots, -S+n. \end{aligned} \tag{5.3b}$$

From these recursion formulas one obtains

$$p_S = J_k\Lambda_k + J_n\Lambda_n + \Gamma p_{-S} \tag{5.4}$$

with

$$\begin{aligned} \Lambda_k =& (w_S^{S-k})^{-1} + (w_{S-k}^{S}/w_S^{S-k})(w_{S-k}^{S-2k})^{-1} + (w_{S-k}^{S}/w_S^{S-k}) \\ &\times (w_{S-2k}^{S-k}/w_{S-k}^{S-2k})(w_{S-2k}^{S-3k})^{-1} + \cdots + (w_{S-k}^{S}/w_S^{S-k}) \\ &\times (w_{S-2k}^{S-k}/w_{S-k}^{S-2k}) \cdots (w_{-hS+k}^{-hS+2k}/w_{-hS+2k}^{-hS+k})(w_{-hS+k}^{hS})^{-1}, \end{aligned}$$

$$\begin{aligned} \Lambda_n =& (w_{S-k}^{S}/w_S^{S-k}) \cdots (w_{-hS}^{-hS+k}/w_{-hS+k}^{-hS}) \\ &\times [(w_{-hS}^{-hS-n})^{-1} + (w_{-hS-n}^{-hS}/w_{-hS}^{-hS-n})(w_{-hS-n}^{-hS-2n})^{-1} \\ &+ \cdots + (w_{-hS-n}^{-hS}/w_{-hS}^{-hS-n}) \cdots (w_{-S+n}^{-S+2n}/w_{-S+2n}^{-S+n}) \\ &\times (w_{-S+n}^{-S})^{-1}] \end{aligned} \tag{5.5}$$

and

$$\begin{aligned} \Gamma =& (w_{S-k}^{S}/w_S^{S-k}) \cdots (w_{-hS}^{-hS+k}/w_{-hS+k}^{-hS})(w_{-hS-n}^{-hS}/w_{-hS}^{-hS-n}) \\ &\times (w_{-S}^{-S+n}/w_{-S+n}^{-S}) \\ =& \exp(\alpha_+)\exp(-\alpha_-). \end{aligned} \tag{5.6}$$

In the calculation of Λ_k and Λ_n we have now to include the electronic matrix elements. Because of Eqs. (5.1)–(5.3), $J_k = J_n$ and therefore p_S - $\Gamma p_{-S} = J_k(\Lambda_k + \Lambda_n)$. With Eq. (5.5) and in complete analogy to Eqs. (4.6)–(4.12) we obtain

$$\begin{aligned} \Lambda_k + \Lambda_n =& \frac{\exp[\alpha_+]}{C(Ak^2)^3} \sum_{i=0}^{S(1+h)/k-1} \exp[-Ak^2(1+i)^2/(k_BT)] \\ &\times \frac{\exp[Ak^2(1+2i)/(k_BT)]-1}{(1+2i)^3|\langle -hS+ki|S_-^k|-hS+k(i+1)\rangle|^2} \\ &+ \frac{\exp(\alpha_+)}{C(An^2)^3} \sum_{i=0}^{S(1-h)/n-1} \exp[-An^2i^2/(k_BT)] \\ &\times \frac{1-\exp[-An^2(1+2i)/(k_BT)]}{(1+2i)^3\langle -hS-n(i+1)|S_-^n|-hS-ni\rangle|^2}. \end{aligned} \tag{5.7}$$

With $C' \equiv C(AS^2)^3$ (cf. Table I) this leads to a general expression for $\tau_\pm$,

$$\begin{aligned} \tau_\pm = \frac{\exp(-\alpha_\pm)}{C'} \Bigg\{ & \left(\frac{S}{k}\right)^6 \sum_{i=0}^{S(1+h)/k-1} \exp\left[-\alpha\left(\frac{k}{S}\right)^2 i^2\right] \\ &\times \frac{1-\exp\left[-\alpha\left(\frac{k}{S}\right)^2(1+2i)\right]}{(1+2i)^3|\langle -hS+ki|S_-^k|-hS+(k(i+1))\rangle|^2} \\ &+ \left(\frac{S}{n}\right)^6 \sum_{i=0}^{S(1-h)/n-1} \exp\left[-\alpha\left(\frac{n}{S}\right)^2 i^2\right] \\ &\times \frac{1-\exp\left[-\alpha\left(\frac{n}{S}\right)^2(1+2i)\right]}{(1+2i)^3\langle -hS-n(i+1)|S_-^n|-hS-ni\rangle|^2} \Bigg\}. \end{aligned} \tag{5.8}$$

The electronic matrix elements contained in Eq. (5.8) depend strongly on the involved quantum numbers. Because of $S_-|S,m\rangle = [S(S+1)-m(m-1)]^{1/2}|S,m-1\rangle$ and $S(S+1) - m(m-1) = (S+m)(S-m+1)$ we can write for the matrix elements

$$\begin{aligned} &|\langle -hS+ki|S_-^k|-hS+k(i+1)\rangle|^2 \\ &\quad = \frac{[S(1+h)-ki]!\,[S(1-h)+k(i+1)]!}{[S(1+h)-k(i+1)]!\,[S(1-h)+ki]!} \end{aligned} \tag{5.9a}$$

and

$$\begin{aligned} &|\langle -hS-n(i+1)|S_-^n|-hS-ni\rangle|^2 \\ &\quad = \frac{[S(1-h)-ni]!\,[S(1+h)+n(i+1)]!}{[S(1-h)-n(i+1)]!\,[S(1+h)+ni]!}. \end{aligned} \tag{5.9b}$$

VI. RESULTS AND DISCUSSION

In order to analize the general expression (5.8) we treat first the case of zero external field. For $h=0$, assuming $k=n$ and introducing Eq. (5.9) in Eq. (5.8) we find

$$\begin{aligned} \tau =& \frac{2\,exp(\alpha)}{C'}\left(\frac{S}{k}\right)^6 \\ &\times \sum_{i=0}^{S/k-1} \frac{(1+2i)^{-3}\exp\left[-\alpha\left(\frac{k}{S}\right)^2 i^2\right]}{\{(S-ki)(S-ki-1)\cdots[S-ki-(k-1)]\}} \\ &\times \frac{1-\exp\left(-\alpha\left(\frac{k}{S}\right)^2(1+2i)\right)}{[(S+ki+k)(S+ki+k-1)\cdots(S+ki+1)]}. \end{aligned} \tag{6.1}$$

We estimate this for several k values. For high k or n values, e.g., for $n=k=S$ (three-level model above) the denominators are of the order $(2S)!$ and thus τ tends to zero. The case $k \neq n$ is not fundamentally different from $k=n$. We start therefore considering $k=n=1$ and estimate τ at

$$\tau > \frac{2\,\exp(\alpha)}{C'} S^6 \frac{1-\exp(-\alpha/S^2)}{S(S+1)} \approx \frac{2\alpha}{C'} S^2 \exp(\alpha). \tag{6.2}$$

In the usual temperature range $T=1-1000$ K, and with KV from Table I, α varies from approximately 2000 to 2 and α/S^2 from 2×10^{-4} to 2×10^{-7} so that we can estimate a lower limit for τ, using the values of Table I, as $\tau \geqslant 8.66 \times 10^{-4}\ \mathrm{s} \cdot (B_1^1/\mathrm{cm}^{-1})^{-2} \alpha \cdot \exp(\alpha)$. In a wide range of B_1^1 this is far too long compared to the experimental values.

For $k=2$ we obtain from Eq. (6.1)

$$\tau = \frac{2\,\exp(\alpha)}{C'} \left(\frac{S}{2}\right)^6 \sum_{i=0}^{S/2-1} \exp(-4\alpha i^2/S^2) \frac{1-\exp[-4\alpha(1+2i)/S^2]}{(1+2i)^3[(S-2i)(S-2i-1)(S+2i+2)(S+2i+1)]}. \tag{6.3}$$

As an upper limit of τ we estimate

$$\tau < (1.6/8C')\,\alpha\,\exp(\alpha) \tag{6.4a}$$

and thus, with the values of Table I,

$$\tau \approx [8.33\times 10^{-12}\ \mathrm{s}/(B_2^2/cm^{-1})^2] \cdot \alpha\,\exp(\alpha). \tag{6.4b}$$

If we concisely write τ^{-1} in the form (6.5) as it is often done assuming a weakly varying prefactor τ_0^{-1} we obtain in the temperature range $1-1000$ K

$$\begin{aligned} \tau^{-1} &\equiv \tau_0^{-1} \exp(-\alpha) \\ &= (6\times 10^{7\cdots 10})\ \ \mathrm{s}^{-1}[B_2^2/cm^{-1}]^2) \cdot \exp(-\alpha) \end{aligned} \tag{6.5}$$

or, e.g., for $T=300$ K ($\alpha=6.45$), where the transition of slow to fast relaxation in the Mössbauer spectra of Ref. 14 occurs, $\tau^{-1} \approx 2.94\times 10^7\ \ \mathrm{s}^{-1}(B_2^2/\mathrm{cm}^{-1})^2$, which for $B_2^2 \leqslant 1$ cm^{-1} would correspond to a completely static Mössbauer pattern.

We have no detailed information on the value of B_2^2. The value $k=2$, i.e., a second-order dynamical spin Hamiltonian, describes normal spin-orbit coupling treated in second-order perturbation theory for which a value of the coupling parameter B_2^2 in the range of 0.2 cm^{-1} for *S*-state ions, e.g., Fe^{3+}, may be adequate.[12] This results in $\tau_0^{-1} \approx 2.4\times 10^{6\cdots 9}\ \ \mathrm{s}^{-1}$ in contrast to the experimental range of $(10^{10\cdots 13})\ \mathrm{s}^{-1}$. However, for Fe^{2+} the coupling constant B_2^2 could be considerably higher, e.g., for $B_2^2 \approx 13$ cm^{-1}, which seems to be in a reasonable range, we would obtain the correct order of magnitude of τ_0^{-1}. In this case $\tau^{-1}(\alpha=6.45) = 5\times 10^9\ \ \mathrm{s}^{-1}$ which corresponds to an intermediate relaxation Mössbauer pattern as experimentally found in Ref. 14.

For comparison we also consider the case of $k=3$ and obtain from Eq. (6.3) the approximation

$$\begin{aligned} \tau &\approx (1/27C'S^2)\,\alpha\,\exp(\alpha) \\ &\approx 1.5\times 10^{-19}\ \ \mathrm{s}(B_3^3/\mathrm{cm}^{-1})^{-2}\alpha\,\exp(\alpha). \end{aligned} \tag{6.6}$$

It seems to be reasonable that the value of the coupling constants decreases strongly with the order of the dynamical spin Hamiltonian involved. If we take, e.g., $B_3^3 = 10^{-4} \cdot B_2^2$ with $B_2^2 = 13\ \ \mathrm{cm}^{-1}$ we obtain for the relaxation rate $\tau_0^{-1} \approx 1.8\times 10^{10\cdots 13}\ \ \mathrm{s}^{-1}$, i.e., the correct order of magnitude. However, for $k>3$ the values of B_l^p needed for obtaining reasonable τ_0 values are unrealistically small. Considering the different B_l^p values above we adopt $k=2$ as a probable value for the order of the dynamical spin Hamiltonian.

An external field is easily included in the calculations. For $k=n=2$ we obtain from Eqs. (5.8) and (5.9) the final result,

$$\tau_{\pm} = C'^{-1} \exp(\alpha_{\pm})(S/2)^6[\sigma(+h)+\sigma(-h)] \tag{6.7}$$

with

$$\sigma(\pm h) = \sum_{i=0}^{(S/2)(1\pm h)-1} \frac{\exp\left[-\alpha\left(\frac{2}{S}\right)^2 i^2\right]}{(1+2i)^3[S(1\pm h)-2i][S(1\pm h)-2i-1]} \frac{1-\exp\left[-\alpha\left(\frac{2}{S}\right)^2(1+2i)\right]}{[S(1\mp h)+2i+2][S(1\mp h)+2i+1]}. \tag{6.8}$$

In complete analogy to the case $h=0$ and in good approximation up to $h \approx 0.95$ we estimate $\tau_{\pm}$ as

$$\tau_{\pm} \approx (0.2C'^{-1})\,\alpha(1-h^2)^{-2}\exp(\alpha_{\pm}). \tag{6.9}$$

In terms of a relaxation rate, with C' from Table I and $B_2^2 = 13\ \mathrm{cm}^{-1}$ this results in our final estimation

$$\tau_{\pm}^{-1} \approx 2\times 10^{13}\ \ \mathrm{s}^{-1}\alpha^{-1}(1-h^2)^2 \exp(-\alpha_{\pm}). \tag{6.10}$$

Comparing Eqs. (6.4)–(6.10) with the formulas (2.3), (2.6), (2.11), and (2.12) given by Néel, Brown, and others, we state that the most prominent feature in τ^{-1}, namely the presence of an Arrhenius-like factor $\exp(-\alpha)$ is also found in our formula. Moreover, since in Eqs. (6.4) and (6.9) τ is proportional to α, the asymptotic behavior at high temperature ($\tau\rightarrow 0$ for $\alpha\rightarrow 0$) is the same as in Eqs. (2.5), (2.7), and (2.12), but different from Eqs. (2.3) and (2.6). Though in principle we can define a single τ only in the low-temperature limit, the formulas that we deduced are meaningful also at higher temperatures.

The field dependence in our formulas is similar to that in Brown's expression. Our $\tau_{\pm}^{-1}$ is proportional to $(1-h^2)(1+h)(1-h)$ whereas $\tau_{\pm Br}^{-1}$ from Eq. (2.6) is proportional to $(1-h^2)(1\pm h)$. For τ_{-}^{-1} the field dependent prefactor terms differ by a factor 2, at most (for $h\rightarrow 1$), and for τ_{+}^{-1} our expression tends slightly faster to zero as Brown's. However $\tau_{\pm}^{-1}(h=1)$ calculated without approximations directly from Eq. (5.8) remains finite, which seems to be more correct physically.

The phonon energies ($h=0$) involved in the spin-transitions range from $E_{\pm S\mp 2}-E_{\pm S}=3.3\times 10^{-23}J$ (step at minimum of barrier potential) to $E_0-E_{\pm 2}=1.03\times 10^{-26}J$ (step near to the top of the barrier). The minimum phonon energy is $E_{phmin}=2.21\times 10^{-22}J$ (cf. Table I). Thus for (direct) transitions near to the top of the barrier phonons with an energy of approximately $5\times 10^{-5}\cdot E_{phmin}$ are necessary. We postulated the presence of such low energy phonons. The frequency of these phonons would be of the order of $10^7-5\times 10^{10}$ s^{-1}. We also believe that there is no correlation problem present as it was raised in Ref. 6. However, within the scope of the above developed model no superparamagnetic relaxation would occur in nanosized magnetic particles that are ideally isolated from each other or from a heat bath.

Once disposing on $\tau_{\pm}^{-1}$ from Eqs. (6.8) or (6.10), one is able, at least in the low-temperature regime, to calculate the corresponding superparamagnetic Mössbauer relaxation pattern. The only ''free'' parameter is the coupling constant B_2^2. This can be done in the simplest case by using the formalisms described in Refs. 9 and 15–17 with an effective spin $S=\frac{1}{2}$. Depending on the absolute values of τ_+ and τ_-, both slow and fast relaxation can be present in the spectrum at the same temperature.[18] When the characteristic time of the Mössbauer method is longer than $\tau_{\pm}$, a static (six-line) spectrum is observed whose splitting is reduced by the factor $(\tau_+-\tau_-)/(\tau_++\tau_-)$. Since our $\tau_{\pm}$ from Eq. (6.10) depends stronger on h than Brown's expression (2.6) and is proportional to α this effect should manifest itself more distinctly than hitherto supposed.

For somewhat higher temperatures the fluctuations of S around the anisotropy directions can be approximately taken into account by diminishing the magnetic splitting as a function of the temperature according to the thermal average value (collective excitations, Ref. 1). The correct way, however, to simulate a Mössbauer spectrum for arbitrary temperature and hyperfine interaction would consist in using the ''real'' spin S in a superoperator formalism like in Refs. 9 or 17, where the relaxation supermatrix would contain the transition probabilities (3.11). Unfortunately, this straightforward procedure is not feasible since the method involves the inversion of a non-Hermitian complex matrix of huge order, vis. 3.3×10^8 in our case ($S=3222$, isotope ^{57}Fe). However, for most superparamagnetic materials the magnetic hyperfine interaction is larger than the electric quadrupole interaction and then in calculating a spectrum the simplified expression (2.9) can be used. With this the inversion of a matrix whose order is only $2S+1$ is required and this is feasible on a workstation.

In real samples most of the assumptions made in the beginning are not fulfilled, but in some cases the simulation of spectra can be easily adapted to the real conditions by summing up discrete spectra, e.g., to obtain powder averages or to introduce size dispersion. However, the presence of various easy directions is more difficult to take into account. Other difficulties remain also, like the influence of the surface and surface-near regions in the particles which may result in different anisotropy constants, hyperfine fields, etc. Particle interaction has been discussed by Mørup and Tronc[19] in terms of magnetic dipole interaction between the particles.

At very low temperature, in principle, there exists the possibility that the spin S fluctuates between states on opposite sides of the barrier, without surmounting it, by ''spin tunneling,'' e.g., by phonon assisted ''macroscopic quantum tunneling'' (MQT).[20,21] It seems, however, that MQT is only present in very small ($S\approx 10-100$) ideal clusters, such as crystals consisting of magnetic molecules.[22,23]

VII. CONCLUSION

The thermally activated superparamagnetic relaxation of the magnetization of small noninteracting identical particles under the influence of an external magnetic field can be described by a spin-phonon-interaction-like model in which the total spin S of the monodomain particle interacts with strain fields of the crystal. Transition probabilities between the S_z levels are calculated on the basis of a dynamical spin Hamiltonian and the Debye model. For low temperatures a two-state relaxation system is considered, where the relaxation occurs between the states $|S\rangle$ and $|-S\rangle$ and relaxation rates $\tau_{\pm}^{-1}$ are introduced and calculated for transitions with constant ΔS_z. It is found that $\Delta S_z=2$ and a spin-phonon coupling constant of 13 cm^{-1} reproduces the experimental values of $\tau_{\pm}^{-1}$. The so deduced expression exhibits the same Arrhenius-like factor and a similar, but somewhat steeper dependence on the external field, as the classical formulas by Néel and Brown, derived on the ground of completely different models. The temperature dependence of the pre-exponential factor of our expression is meaningful also for high temperatures. It is possible, on the basis of the spin-transition probabilities introduced, to calculate Mössbauer spectra valid at arbitrary temperatures.

ACKNOWLEDGMENTS

The support of FAPEMIG, CAPES, and CNPq is gratefully acknowledged. One of us, H.D.P., is grateful to Professor G. Langouche and Dr. J. Dekoster from the IKS, Katholieke Universiteit Leuven, and Professor W. Keune from the Gerhard Mercartor Universität Duisburg for the hospitality during a research stay at these institutions.

[1] S. Mørup, J.A. Dumesic, and H. Topsøe, in *Applications of Mössbauer Spectroscopy*, edited by R.L. Cohen (Academic Press, New York, 1980), Vol. II.

[2] J.L. Dormann, Rev. Phys. Appl. **16**, 275 (1981).

[3] H.D. Pfannes, Hyperfine Interact. **110**, 127 (1997).

[4] L. Néel, Ann. Geophys. (C.N.R.S.) **5**, 99 (1949).

[5] W.F. Brown, Jr., Phys. Rev. **130**, 1677 (1963).

[6] D.H. Jones and K.K.P. Srivastava, J. Magn. Magn. Mater. **78**, 320 (1989).

[7] L. Bessais, L. Ben Jaffel, and J.L. Dormann, Phys. Rev. B **45**, 7805 (1992).

[8] D.H. Jones and K.K.P. Srivastava, Phys. Rev. B **34**, 7542 (1986).

[9] H.D. Pfannes and R. Magalhães-Paniago, Hyperfine Interact. **83**, 79 (1994).

[10] J. Villain, F. Hartmann-Boutron, R. Sessoli, and A. Rettori, Europhys. Lett. **27**, 159 (1994).

[11] R. Orbach, and H.J. Stapleton, in *Electron Paramagnetic Resonance*, edited by S. Geschwind (Plenum Press, New York, 1972).

[12] K.K.P. Srivastava and S.N. Mishra, Phys. Status Solidi B **100**, 65 (1980).

[13] N. G. van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1981).

[14] H.D. Pfannes, J.H. Dias Filho, J.L. López, S.L. Pereira, P.C. Morais, and F.A. Tourinho, Hyperfine Interact. **113**, 507 (1998).

[15] H.H. Wickmann, in *Mössbauer Effect Methodology*, edited by I.J. Gruvermann (Plenum Press, New York, 1966), Vol. 2.

[16] M. Blume and J.A. Tjon, Phys. Rev. **165**, 446 (1968).

[17] M.J. Clauser and M. Blume, Phys. Rev. B **3**, 583 (1971).

[18] D.G. Rancourt and J.M. Daniels, Phys. Rev. B **29**, 2410 (1984).

[19] S. Mørup and E. Tronc, Phys. Rev. Lett. **72**, 3278 (1994).

[20] P.C.E. Stamp, E.M. Chudnovsky, and B. Barbara, Int. J. Mod. Phys. B **6**, 1355 (1992).

[21] A. Garg, J. Appl. Phys. **76**, 6168 (1994).

[22] J.R. Friedman, M.P. Sarachik, J. Tejada, and R. Ziolo, Phys. Rev. Lett. **76**, 3830 (1996).

[23] S. Gider, D.D. Awschalom, T. Douglas, S. Mann, and M. Chaparala, Science **268**, 77 (1995).