The theory of superparamagnetic relaxation: Mossbauer study

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Abstract
A theoretical model has been developed to calculate the superparamagnetic relaxation rate for small magnetically ordered particles of uniaxial symmetry having size 50–120 Å. On a microscopic level the relaxation process involves an exchange of energy between magnon and phonon sub-systems via magnon–phonon scattering induced by dynamic exchange. The model has been applied to ultra-fine iron compounds and the calculated superparamagnetic relaxation rates at low temperatures are usually consistent with those which are frequently observed by Mossbauer spectroscopy. One finds that the relaxation rate increases with temperature in a complicated manner besides its dependence on the number of magnetic ions in the particle.

1. Introduction

The Mossbauer spectra of small magnetic particles of α-Fe_2O_3 [1], Fe_3O_4 [2], ferrihydrite [3], ferritins [4] etc at low temperatures often show the presence of magnetic relaxation which is strongly dependent on temperature and particle size. Such particles, which consist of a single magnetic domain, are usually known as superparamagnets and the thermal fluctuation of their magnetization as superparamagnetic relaxation. The shape of the magnetic hyperfine spectra depends upon the rate of fluctuation (i.e. the relaxation rate) of the magnetization vector along possible directions. In ^{57}Fe Mossbauer experiments the effect of magnetic relaxation on spectra can be observed only when the relaxation time (which is the inverse of the relaxation rate) is comparable to the lifetime of the nuclear decay and accordingly the magnetic relaxation rates which affect the lineshape fall within the window 10^7–10^9 s^{-1}. For relaxation rates below the lower limit one usually observes a sharp magnetic sextet and for rates above the upper limit the magnetic interaction is washed out. These small particles fall within the family of 'nano-particles' with dimensions of about 50–150 Å only and their study through different physical techniques has assumed importance in recent years, and therefore it is desirable to examine the interactions which produce magnetic relaxation and this might prove helpful in other areas as well.

In the standard theory of superparamagnetic relaxation for particles with uniaxial symmetry, the magnetization vector randomly jumps between two directions ($\theta = 0, \pi$) corresponding to the energy minima of the system, where the energy of the particle is conveniently expressed as [5, 6]

$$E = -KV \cos^2 \theta - HM_S \cos \theta \tag{1}$$

where K = anisotropy energy per unit volume, V = volume of the particle, M_S = net magnetization of the particle, θ = angle between the magnetization vector and the anisotropy axis and H = magnetic field along the anisotropy axis. The theories given by Brown [5] and Aharoni [7] treat the problem basically as flip–flops between two directions (or energy states for $\theta = 0, \pi$) separated by the anisotropy potential barrier and the relaxation rate is given as

$$R = R_0 \exp(-KV/k_B T) \tag{2}$$

where the pre-exponential factor R_0 is taken to be of the order of 10^{10}–10^{11} s^{-1}. Quite often the same expression is written in terms of relaxation time (τ) as

$$\tau = \tau_0 \exp(KV/k_B T) \tag{3}$$

where the pre-exponential factor τ_0 may be of the order of 10^{-10}–10^{-11} s. It is relevant to mention that for small magnetic particles or micromagnets the anisotropy energy basically arises from 'exchange anisotropy' and 'shape anisotropy'. The exchange anisotropy is an interfacial effect between two magnetic subsystems specially where the interaction is between an antiferromagnetic and a ferromagnetic material, whereas the shape anisotropy is related to surface effects [8].

In an earlier paper by Jones and Srivastava [9] a many-state relaxation model, where all possible orientations of M_S are included, was considered using the stochastic theory of Blume and Tjon [10] and the expression for the Mossbauer line shape function was derived. In a special case the many-state relaxation model reduces to Brown's two level picture [5]. The basic limitations of the existing theories is the absence of any description of the microscopic process which is responsible for causing the superparamagnetic relaxation and this point was also emphasized earlier [9, 11, 12]. Until now the interaction between the particle and its environment has been expressed in terms of a rapidly fluctuating random magnetic field which is inadequate from a microscopic point of view. Even classically it will be difficult to quantify such random magnetic fields and their temperature profile.

It is therefore desirable to develop the microscopic interaction Hamiltonian (or the perturbation potential) which causes the superparamagnetic relaxation so that its rate can be easily calculated, and naturally such an interaction should take into account the dynamics of spin fluctuations and lattice vibrations. This will simply lead to a coupling between spin waves and lattice waves or in other words a coupling between magnons and phonons for the given particle. Akhiezer [13] has shown that the interaction between spin waves and lattice vibrations is quite important for the relaxation process within magnetic crystals at low temperatures. This interaction, commonly known as magnon–phonon interaction, represents the thermal modulation of the Heisenberg exchange interaction between nearest neighbours by lattice vibrations and it causes the exchange (or flow) of energy between magnon and phonon sub-systems. Such an exchange of energy produces a change in the spin-state of the magnetic crystal and hence gives rise to magnetic relaxation. The method developed by Akhiezer [13] and used by Sinha and Upadhyaya [14] for iron compounds will be followed with necessary approximations relevant to the system.

2. Static crystal field scheme

In a static crystal with no lattice vibrations, we consider one localized 3d electron of a magnetic ion. The Hamiltonian for the ith electron is given by

$$H = H_0 + V_0 + H_e + H_a + H_z \tag{4}$$

where $H_0 = p_i^2/2m + U(r_i - R_m^0) =$ free ion Hamiltonian, $V_0 = \sum_{n \neq m} U(r_i - R_n^0) =$ crystal field potential (usual for iron group ions), $H_e =$ exchange interaction between the electrons of the nearest neighbours, $H_a =$ anisotropy interaction and $H_z =$ Zeeman interaction.

In the above description r_i is the position coordinate of the ith electron belonging to the mth ion at R_m^0 and R_n^0 is the position of the nth nearest neighbour ion. In the static crystal field potential the orbital wavefunctions of an electron are solutions of the equation given by

$$(H_0 + V_0)\Phi_\alpha = E_\alpha \Phi_\alpha \tag{5}$$

where the label α represents a particular orbital state. The five orbital wavefunctions of a 3d electron in an octahedral or cubic crystal field are well known [16]. In the case of an Fe(3+) ion, each of the five 3d-orbitals is occupied by one electron and consequently it behaves like a ^{6}S-state ion.

The exchange integral between two electrons of the nearest neighbour ions is given by

$$J_o(R_{mn}^0) = \langle \Phi_{\alpha,m}(r_1)\Phi_{\alpha,n}(r_2)|(e^2/r_{12})|\Phi_{\alpha,n}(r_1)\Phi_{\alpha,m}(r_2)\rangle \tag{6}$$

where $r_{12} = r_1 - r_2$ and $R_{mn}^0 = R_n^0 - R_m^0$. The exchange interaction is finally given by

$$H_e = -2 \sum_{n>m} J_o(R_{mn}^0) S_m S_n \tag{7}$$

where S_m and S_n are the net electronic spins at ions m and n, and the summation extends over all the nearest neighbours. This is the effective exchange interaction which gives rise to magnetic ordering.

3. Dynamic crystal scheme

The lattice vibrations produce an oscillating crystal field potential due to relative displacements of the nearest neighbours and the first order term (V') is given by

$$V' = \sum_m (\partial V/\partial R_{mn})_0 \, dR_{mn} \tag{8}$$

where $R_{mn} = R_m - R_n = R_{mn}^0 + dR_{mn}$. This oscillating field can mix the excited orbital states into the ground orbital state of the magnetic ion, which in turn modulates the exchange interaction. The modified orbital wavefunction can be given by [14, 15]

$$\Psi_\alpha = \phi_\alpha + \sum_\beta (\langle \phi_\alpha|V'|\phi_\beta\rangle)/(E_\alpha - E_\beta) \tag{9}$$

where E_α and E_β are the energies of the states ϕ_α and ϕ_β. In the present case ϕ_α is one of the appropriate 3d orbitals and ϕ_β will be an empty 4p orbital of the Fe(3+) ion. For this modified wavefunction the exchange integral becomes equal to

$$J(R_{mn}) = J_0(R_{mn}^0) + J'(R_{mn}) \, dR_{mn} \tag{10}$$

where $J'(R_{mn}) = 4 \sum \langle \Phi_{\alpha,m}(r_1)\Phi_{\alpha,n}(r_2)|(e^2/r_{12})|\Phi_{\alpha,n}(r_1)\Phi_{\beta,m}(r_2)\rangle$

$$\langle \Phi_{\beta,m}(r_2)|(\partial V/\partial R_{mn})|\Phi_{\alpha,m}(r_2)\rangle/(E_\alpha - E_\beta). \tag{11}$$

The first term of the expression (9) represents the usual exchange integral for the static crystal and the second term arises due to lattice vibrations [14, 15]. Thus the modulated exchange interaction can be expressed as

$$H'_e = -2 \sum_{n>m} [J'(R_{mn})\, \mathrm{d}R_{mn}] S_m S_n. \tag{12}$$

This is the interaction which is responsible for the coupling between electronic spins and lattice vibrations in a magnetically ordered crystal. The parameter J' may be regarded as the gradient of J with respect to separation between magnetic ions (i.e. $J'(R_{mn}) = \mathrm{d}J/\mathrm{d}R_{mn}$).

4. Magnon–phonon interaction

The magnon–phonon interaction Hamiltonian is easily obtained from (11) when the ionic displacements are expressed in terms of phonon operators and the spin operators are expressed in terms of magnon operators, that is, when the quantum mechanical representations are introduced. Using Holstein–Primakoff formalism [17, 18] and retaining only those terms which are linear and bilinear in magnon variables one may write

$$S_+^m = (2S/N)^{1/2} \sum_q \exp(-iq R_m^0) b_q, \qquad S_-^m = (2S/N)^{1/2} \sum_q \exp(-iq R_m^0) b_q^*,$$

and

$$S_z = S - (1/N) \sum_{q,q'} \exp[i(q' - q) R_m^0] b_{q'}^* b_q \tag{13}$$

where b_q and b_q^* are the magnon annihilation and creation operators, (q, q') are the magnon wavevectors, S is the spin of each ion and N is the total number of magnetic ions. Similar transformations can be written for the spin of the nth ion bearing in mind that its position coordinate is R_n^0. Using the above transformations one obtains that

$$S_m S_n = S^2 + (S/N) \sum_{q,q'} [\exp(-iqa) - 1][\exp(iq'a) - 1] b_{q'}^* b_q \tag{14}$$

where $R_n^0 - R_m^0 = a$ is the separation between nearest neighbours (or lattice constant) and the mth ion is supposed to be at the origin. For the whole crystal the above expression is summed over the possible number of magnetic interactions $Nz/2$ where z is the number of nearest neighbours in the given structure and N is the total number of magnetic ions.

The lattice waves are included by expressing the ionic displacements in terms of phonon annihilation and creation operators. A small displacement δR_m of the mth ion is given by

$$\delta R_m = (1/N)^{1/2} \sum_k (\hbar/2M\omega_k)^{1/2} i(a_k^* - a_{-k}) \exp(ik R_m^0) \tag{15}$$

where a_k and a_k^* are phonon annihilation and creation operators respectively, $k = $ phonon wavevector, $\omega_k = $ frequency of phonon with wavevector k and $M = $ mass of the ion. A similar expression can be given for the displacement δR_n of the nth ion. Thus one obtains that

$$\mathrm{d}R_{mn} = (1/N)^{1/2} \sum_k (\hbar/2M\omega_k)^{1/2} i(a_k^* - a_{-k})[\exp(ika) - 1] \tag{16}$$

where $\mathrm{d}R_{mn} = \delta R_n - \delta R_m$, and again the mth ion is supposed to be at the origin $R_m^0 = 0$. The Hamiltonian for the magnon–phonon interaction (H_{mp}) is obtained by using (13) and (15) in the expression (11) as

$$H_{mp} = -i(2J'S) \sum_{q,q',k} (\hbar/2NM\omega_k)^{1/2} [\exp(ika) - 1]$$

$$\times [\exp(-iqa) - 1][\exp(iq'a) - 1] b_{q'}^* b_q (a_k^* - a_{-k}) \tag{17}$$

where the terms containing phonon operators only have been dropped (because these do not represent magnon–phonon coupling) and (14) has been multiplied by N to take into account the whole crystal. These interaction terms represent two-magnon one-phonon inelastic scattering processes. They indicate that a magnon of wavevector q is annihilated and another magnon of wavevector q' is created with the emission (or absorption) of one phonon with wavevector k (or $-k$). The scattering of higher orders, for example those involving two-magnon two-phonon processes, have been ignored [13, 19]. The expression (17) differs from that used earlier [13, 14] (though the methodology is very similar) as in the present formulation the general form of the exchange term which contains both q and q' in (13) has been used. Now for a pair of nearest neighbours under the long wavelength approximation one obtains that

$$[\exp(ika) - 1][\exp(-iqa) - 1][\exp(iq'a) - 1] = ikqq'a^3. \tag{18}$$

Thus the expression (17) for the magnon–phonon interaction Hamiltonian may be written as

$$H_{mp} = \sum_{q,k} C(q, k)[b_{q-k}^* b_q (a_k^* - a_{-k})] \tag{19}$$

where

$$C(q, k) = (2SJ'a^3)(\hbar/2NM\omega_k)^{1/2} q(q - k)k. \tag{20}$$

5. Transition probability

The eigenstates of the system can be represented in terms of the product of magnon and phonon occupation numbers. Thus the initial and final states may be written as $\Psi_i = |n_q, n_{q-k}, N_k\rangle$ with energy $= E_i$ and $\Psi_f = |n_q', n_{q-k}', N_k'\rangle$ with energy $= E_f$, where n and N refer to magnon and phonon occupation numbers given by the respective Bose–Einstein distributions. The transition probability (W) per unit time is given by the standard expression in quantum mechanics as

$$W = (2\pi/\hbar)|\langle \Psi_i|H_{mp}|\Psi_f\rangle|^2 \delta(E_i - E_f). \tag{21}$$

It can be seen that during these transitions the total number of magnons remains unchanged but the number of phonons changes. The probability (W) in fact gives the rate of change of the number of phonons. Using the properties of magnon and phonon operators and taking the difference of the transition probabilities in two directions, one obtains that

$$\langle \dot{N}_k \rangle = (2\pi/\hbar) \sum_q |C(q, k)|^2 [(n_{q-k} + 1)n_q(N_k + 1) - n_{q-k}(n_q + 1)N_k]\delta(E_{q-k} - E_q + E_k) \tag{22}$$

where E_{q-k} and E_q are the energies of the magnons with wavevectors $q - k$ and q respectively, and E_k is the energy of the phonons with wavevector k. The delta function ensures energy conservation during transition. The rate of transfer of energy between magnon and phonon sub-systems is given by

$$\dot{Q} = \sum_k \hbar\omega_k \langle \dot{N}_k \rangle. \tag{23}$$

It is implied, as in [13, 14], that the magnon and phonon sub-systems have different temperatures usually known as spin temperature (T_S) and lattice temperature (T). This means that n_q and N_k are expressed in terms of T_S and T respectively. Assuming that $T_S - T = \Delta T$ is small, the magnon number can be expressed in terms of T [13] by the method of Taylor series expansion, and then one may write

$$\exp(E_q/k_B T_S) = \exp(E_q/k_B T)[1 - (E_q/k_B T^2)\Delta T] \tag{24}$$

and a similar expression for $\exp(E_{q-k}/k_B T_S)$. Using the energy conservation relation $E_q - E_{q-k} = E_k = \hbar\omega_k$ and replacing the summation by integration for the continuous magnon and phonon spectra one obtains that

$$\dot{Q} = (2\pi/\hbar) \iint dq\,dk\,|C(q,k)|^2 (\hbar\omega_k)^2 (\Delta T/k_B T^2)$$
$$\times \frac{\exp(E_q/k_B T)g(k)g(q)\delta(E_q - E_{q-k} - E_k)}{[\exp(E_{q-k}/k_B T) - 1][\exp(E_q/k_B T) - 1][\exp(E_k/k_B T) - 1]} \tag{25}$$

where $T = T_S$ has been used for the magnon terms in the denominator, $g(k) =$ density of phonon states and $g(q) =$ density of magnon states. For example, the magnon occupation number $(n_q + 1)$ becomes

$$n_q + 1 = \exp(E_q/k_B T_S)/[\exp(E_q/k_B T_S) - 1]$$
$$= \exp(E_q/k_B T)[1 - E_q(\Delta T/k_B T^2)]/[\exp(E_q/k_B T) - 1]. \tag{26}$$

For the Debye type spectra one may use

$$g(k)\,dk = 3(Na^3/2\pi^2)k^2\,dk, \qquad \text{and} \qquad g(q)\,dq = (Na^3/2\pi^2)q^2\,dq \tag{27}$$

where Na^3 is the volume (V) of the crystal and the factor of three in $g(k)$ accounts for three directions of polarization. As per thermodynamics the change of energy and the temperature of the lattice and spin sub-systems are related by the following equations:

$$dT/dt = \dot{Q}/C_p, \qquad \text{and} \qquad dT_S/dt = -\dot{Q}/C_m \tag{28}$$

where T and T_S are the lattice and spin temperatures, and C_p and C_m are the specific heats of the phonon and magnon sub-systems. One may use the relation $d(T - T_S)/dt = \Delta T/\delta t = \Delta T/\tau_{mp}$, which simply means that the transfer of energy within the sub-systems having temperature difference ΔT takes place within the time interval δt or the relaxation time τ_{mp}. Then from (27) one immediately obtains that

$$1/\tau_{mp} = [(1/C_m) + (1/C_p)](\dot{Q}/\Delta T). \tag{29}$$

It indicates that the magnon–phonon relaxation rate $(1/\tau_{mp})$ depends both on the lattice dynamic and magnetic properties of the crystal.

6. Superparamagnetic particles

The discussion presented above applies to any magnetic system in general. The difference lies in the magnon energy spectrum for the given system. Here we consider a ferromagnetically ordered superparamagnetic particle. The energy of magnons will consist of the exchange, anisotropy and Zeeman terms. The magnon energy (E_s) due to ferromagnetic excitations (or spin waves) is given by the standard relation [18]

$$E_s = \sum_q (2J_0 S q^2 a^2) b_q^* b_q = \sum_q (k_B T_C q^2 a^2) b_q^* b_q \tag{30}$$

where in terms of Curie temperature (θ_C) the exchange constant $J_0 = 3k_B\theta_C/2zS(S+1)$, $z =$ number of nearest neighbours [20] and for convenience we put $T_C = 3\theta_C/z(S+1)$. It is seen that $T_C = \theta_C$ for $z = 2$, $S = 1/2$ and the completely ordered state (ground state with no magnons) is considered to have zero energy. For Fe(3+) in octahedral coordination $(S = 5/2, z = 6)$ one gets $T_C = \theta_C/7$.

Now it is desirable to express the energy of the superparamagnetic particle given by expression (1) in terms of magnon operators, which can be done by writing the spin operators in terms of magnon variables through the following representations [18]:

$$S^2 = NS(NS + 1) \approx (NS)^2 \qquad \text{and} \qquad S_Z = NS - \sum_q b_q^* b_q,$$

where $S = NS$, and then one may write

$$\cos^2\theta = (S_Z/S)^2 \approx 1 - (2/NS)\sum_q b_q^* b_q \tag{31}$$

neglecting the higher order term $(b_q^* b_q)^2$ which is small at low temperatures. The anisotropy and Zeeman energy terms of the particle given in expression (1) are then reduced to the form

$$E = -A_0 + (2KV/NS + g\beta_e H)\sum_q b_q^* b_q \tag{32}$$

where $A_0 = KV + g\beta_e\,HNS$, which is the anisotropy and Zeeman energy of all the magnetic ions. The completely ordered magnetic state with no magnon (or no spin wave) has the energy $-A_0$, which is the depth of the anisotropy potential well and its value is equal to $-KV$ when no magnetic field is applied. Similarly one may write $B_0 = 2KV/NS + g\beta_e H$, which is the anisotropy and Zeeman energy of a single magnetic ion only. Thus the total energy (E_m) of the magnon gas (or magnon sub-system) for a superparamagnetic particle is given by

$$E_m = \sum_q E_q b_q^* b_q = -A_0 + \sum_q [B_0 + k_B T_C q^2 a^2] b_q^* b_q. \tag{33}$$

This is an important expression in the sense that it indicates how the dimension of the particle and its potential/anisotropy energy comes into the magnon dispersion relation. The energy of the phonons (E_p) is also given by the standard relation [20] as

$$E_p = \sum_k E_k a^* a_k = \sum_k (k_B T_D ka) a^* a_k \tag{34}$$

where $T_D = \theta_D/(6\pi^2)^{1/3} \approx \theta_D/4$, and θ_D is the Debye temperature of the crystal.

7. Evaluation of $\dot{Q}$

The expression for $\dot{Q}$ is to be integrated after inserting the values of $C(k,q)$, $g(k)$, $g(q)$ and using $\hbar\omega_k = k_B T_D ka$ for the phonon energy in expression (25) which gives

$$\dot{Q} = (3N\hbar/4M\pi^3)(2J'S)^2(T_D\Delta T/T^2)\iint dq\,dk\,q^4(q-k)^2 k^5 a^{13}$$
$$\times f(E_q)f(E_{q-k})f(E_k)\exp(E_q/k_B T)\delta(E_q - E_{q-k} - E_k) \tag{35}$$

where $f(E) = [\exp(E/k_B T) - 1]^{-1}$ represents the Bose–Einstein distribution for magnons and phonons of respective energies E_q, E_{q-k} and E_k. Using the dimensionless variables $x = ka$ and $y = qa$ the above integral reduces to

$$\iint dy\,dx\,y^4(y-x)^2 x^5 f(E_q)f(E_{q-k})f(E_k)\exp(E_q/k_B T)\delta(E_q - E_{q-k} - E_k). \tag{36}$$

The delta function is first written in terms of the new variables using $E_q = k_B T_C y^2$, $E_{q-k} = k_B T_C(y-x)^2$ and $E_k = k_B T_D x$, which gives

$$\delta(E_q - E_{q-k} - E_k) = \delta[2k_B T_C x((y - x/2) - T_D/2T_C)] = (1/2k_B T_C x)\delta(y - (x+\alpha)/2), \tag{37}$$

where $\alpha = T_D/T_C$. The integration over y yields a non-zero value for the condition $y = (x + \alpha)/2$ only and thus the integral reduces to

$$(1/2^7 k_B T_C)\int dx\,x^4(x+\alpha)^4(x-\alpha)^2 f(E_q)f(E_{q-k})f(E_k)\exp(E_q/k_B T). \tag{38}$$

This integral cannot be solved in a closed manner and therefore further approximations especially at low temperatures will be made. At low temperatures (long wavelengths) x and y (like k and q) will be small and therefore the following substitutions can be made:

$$(x + \alpha) \to \alpha, (x - \alpha) \to -\alpha, \qquad f(E_{q-k}) \to f(E_q) \quad \text{and} \quad f(E_q) \approx \exp(-E_q/k_B T).$$
(39)

Then the expression (38) will contain only one $\exp(-E_q/k_B T)$ related to magnon energy and under the condition $y = (x + \alpha)/2 \to \alpha/2$ it may be expressed as

$$\exp(-E_q/k_B T) = \exp(-A) \exp(-B) \exp(-T_D^2/4TT_C)$$
(40)

where

$$B = (2KV/NS + g\beta_e H)/k_B T \qquad \text{and} \qquad A = (KV + g\beta_e HNS)/k_B T.$$
(41)

It is obvious that B is proportional to the energy of one magnetic ion whereas A is proportional to the energy of all magnetic ions (whole particle) and therefore the latter is much larger than the former. As a consequence it is the term $\exp(-A)$ which always dominates over the term $\exp(-B)$ and this will become apparent when doing quantitative calculations. Since the term $\exp(-E_q/k_B T)$ reduces to the form (40) which does not contain the phonon variable x, it comes out of the integral and then (38) reduces to

$$(1/2^7 k_B T_C)(\alpha^6) \exp(-T_D^2/4TT_C) \exp(-A) \exp(-B) \int \mathrm{d}x \, x^4 [\exp(xT_D/T) - 1]^{-1}.$$
(42)

This integral on the phonon spectrum can be evaluated at low temperatures within the limits 0 to ∞ as

$$\int \mathrm{d}x \, x^4 [\exp(xT_D/T) - 1]^{-1} = (T/T_D)^5 \int \mathrm{d}z \, z^4 [\exp(z) - 1]^{-1} = (T/T_D)^5 [4! \zeta(5)]$$
(43)

where the Riemann zeta function $\zeta(5) = 1.0369 \approx 1$. Considering all these values the double integral is evaluated and the expression (35) is finally given as

$$\dot{Q} = (9N\hbar/64M\pi^2)(2J'S)^2(T_D^2/T_C^7)(T^3)(\Delta T/k_B) \exp(-T_D^2/4T_C T) \exp(-A) \exp(-B).$$
(44)

The terms $\exp(-A)$ and $\exp(-B)$ have been kept separate to indicate the role they play. For ferromagnets $K = 0$ and then both these terms become unity when $H = 0$, which amounts to saying that for large particles the anisotropy has negligible effect. The result (44) is a new one and it differs from the earlier derivations [13, 14].

8. Expression for relaxation rate

In order to obtain the expression for relaxation rate $(1/\tau_{mp})$ the values of C_m and C_p are required. Since our aim is to calculate the specific heat of magnon gas (C_m) it is only the temperature-dependent (i.e. q-dependent) energy of magnons that is required (i.e. constant terms A_0 and B_0 are dropped) in the following standard expression [18]:

$$E_m = \int \mathrm{d}q \, E_q g(q)/[\exp(E_q/k_B T) - 1].$$
(45)

Its evaluation involves $\Gamma(5/2)\zeta(5/2)$, the product of gamma and Riemann zeta functions, whose standard values are $\Gamma(5/2) = 3\pi^{1/2}/4$ and $\zeta(5/2) = 1.341$ for the limits 0 to ∞. At low temperatures and $H = 0$ it is quite safe to adopt the standard result given by [18]

$$C_m = 0.113 N k_B (T/\theta_C)^{3/2}.$$
(46)

The specific heat of phonons having Debye type spectrum is given by another standard relation as [20]

$$C_p = (12\pi^4 N k_B/5)(T/\theta_D)^3. \tag{47}$$

Using the values of $\dot{Q}$, C_m and C_p in expression (29) the superparamagnetic relaxation rate $(1/\tau_{sp})$ for the magnon–phonon scattering process is finally given by

$$1/\tau_{sp} = (9\hbar/64M\pi^2)(2J'S)^2(T_D^2/T_C^7)(T^3/k_B^2)\exp(-T_D^2/4T_C T)$$
$$\times [8.85(\theta_C/T)^{3/2} + (5/12\pi^4)(\theta_D/T)^3]\exp(-A). \tag{48}$$

Here the nomenclature has been slightly changed by using the notation $1/\tau_{sp}$ for superparamagnets in the place of the usual $1/\tau_{mp}$ for ferromagnets. As $A \gg B$ it is sufficient to retain the term $\exp(-A)$ only. The above expression may be recast in the familiar form as $1/\tau_{sp} = R_0(T)\exp(-KV/k_B T)$, where

$$R_0(T) = (9\hbar/64M\pi^2)(2J'S)^2(T_D^2/T_C^7)(T^3/k_B^2)\exp(-T_D^2/4T_C T)$$
$$\times [8.85(\theta_C/T)^{3/2} + (5/12\pi^4)(\theta_D/T)^3]. \tag{49}$$

It is this pre-exponential factor which has remained almost unexplored but it is the most important component of the superparamagnetic relaxation theory. It shows that $R_0(T)$ is substantially temperature dependent in a complicated manner.

9. Dynamic exchange parameter (J')

The dynamic exchange parameter $J'(R_{mn})$ for iron compounds may depend on the electronic orbitals which are involved in the bonding mechanism. In the case of Fe(3+) systems it is the $3d_z^2$ orbital of Fe(3+) and the $2p_z$ orbital of the oxygen ligand which provides most of the bonding and consequently the relative displacements between these ions (O–Fe–O) along the z direction produce most of the oscillating crystal field potential which essentially mixes the empty 4p orbital into the 3d orbital of Fe(3+) for an odd vibration. The value of the exchange integral $J(R_{mn})$ for iron compounds has been estimated to be of the order of 0.27 eV by Koide *et al* [21] but realistically taken as 0.1 eV [14]. For ferromagnetic iron ($S = 1$, $\theta_C = 1040$ K) the value of $J = 0.012$ eV as estimated through the standard relation which connects these quantities [20]. The iron oxides usually have a smaller Curie temperature and higher ionic spin that might suggest a lower exchange constant. In fact for ferrimagnetic Fe_3O_4 the value of exchange constant $J \approx 21$ K or 2.0×10^{-3} eV only [22] and a few other Fe-based ferrimagnets also give similar values [23]. It is therefore realistic to take $J \approx 2.0 \times 10^{-3}$ eV for the group of ultra-fine iron oxides under consideration.

The potential energy of an electron at the central ion of the collinear O–Fe–O chain may be taken as $V = (-Ze^2)[(R_0 - r)^{-1} + (R_0 + r)^{-1}]$, where R_0 is the equilibrium separation of neighbours from the central ion and r is the position coordinate of the electron with respect to the central ion which has charge $+Ze$. This gives $(dV/dR) = (dV/dr) = (4Ze^2 r/R_0^3)$. Using $r \approx 1$ Å as the mean radius of a 3d electronic orbital and $R_0 \approx 2.5$ Å, one obtains that $dV/dr = 1.77 \times 10^{-3}$ erg cm^{-1} which is equal to $\langle 3d_{z2}|dV/dR|4p_z \rangle$ as well within an order of magnitude [14].

The value $E_\alpha - E_\beta$ (or $E_{3d} - E_{4p}$) for Fe-series metals lies in the range 5–10 eV but it has been considered safe to take $E_{3d} - E_{4p} \approx 10$ eV for iron [14] and we accept the same. Using the above estimates one finally obtains that $J'(R_{mn}) = 2.12 \times 10^{-6}$ erg cm^{-1}. The value of J' may differ from system to system by a significant factor and hence the above value provides only an initial estimate. It may not be out of context to mention that for structurally similar oxygen bridged copper compounds the estimated $J' = 5 \times 10^{-5}$ erg cm^{-1} [24] and so the above estimate appears reasonable within an order of magnitude.

10. Estimation of relaxation rates

The calculation of relaxation rates requires the knowledge of several physical parameters which have to be estimated from different experimental data that may be most suited to the given compounds. First comes the estimation of θ_D, θ_C and K for iron compounds/oxides. These magnetic systems are antiferromagnetic (i.e. goethite), weakly ferromagnetic (i.e. α-Fe_2O_3 above the Morin transition temperature), ferrimagnetic (i.e. Fe_3O_4) or of uncertain magnetic structure (i.e. ferryhydrite). Surface effects may further complicate their magnetic structure and lead to partial spin ordering. In general each magnetic structure may lead to a different dispersion relation of its own and produce somewhat different magnetic relaxation rate. Also, where sub-lattices exist there may be a possibility of relaxation between the sub-lattices if the exchange coupling is not strong, etc. These examples and considerations simply indicate the difficulty in dealing with the problem in a quantitative manner.

For the present we assume that ultra-fine iron oxide particles are essentially antiferromagnetic and the exchange coupling is strong. In this situation the relaxation of the antiferromagnetic moment will be similar to that of the ferromagnetic moment in zero applied field. For α-Fe_2O_3 lattice $\theta_D \sim 700$ K [25], $\theta_C \sim 950$ K [26] and for Fe_3O_4 lattice $\theta_D \sim 650$ K [25], $\theta_C \sim 850$ K [27]. Therefore, one may take $\theta_D \approx 700$ K and $\theta_C \approx 900$ K as representative values for the calculation of the relaxation rates. Their lattice constant $a \approx 5$ Å for which the volume of the unit cell $a^3 = V/N \approx 1.25 \times 10^{-22}$ cm^3 (for simple cubic structure). For bcc and fcc structures care should be taken to correlate V and N. For an Fe(3+) ion $M = 56 \times 1.66 \times 10^{-24}$ gm and spin $S = 5/2$.

The magnetic anisotropy energy has been measured in various systems [27] including Fe(2+) and Fe(3+) compounds like pyrrhotite (FeS to Fe_6S_7) and magnetite (Fe_3O_4). In general the anisotropy energy is temperature dependent and its sign can also change. For cubic magnetite the anisotropy constant $K \approx 10^5$ erg cm^{-3} and for hexagonal pyrrhotite $K = 2 \times 10^5$ to 5×10^6 erg cm^{-3} depending upon the direction of magnetization [27]. Though these measurements have been made on bulk materials, it may not be unreasonable to assume a similar value of anisotropy constant for small particles too if the anisotropy arises mainly from the microscopic interactions such as spin–orbit, exchange, dipolar and crystal field interactions [6, 27]. For very small particles the non-symmetrical shape and surface effects can appreciably contribute to the anisotropy energy, but these may not change its order of magnitude. For the present it is assumed that the anisotropy constant $K \approx 10^5$ erg cm^{-3} and it is temperature independent. This translates into $K \approx 1.25 \times 10^{-17}$ erg or ≈ 0.1 K per magnetic ion. Using the above data relaxation rates have been calculated for $H = 0$ for varying number of magnetic ions ($N = 500, 1000, 3000, 5000$ and 7000) and given in table 1. The particle size can also be expressed in terms of its volume or in terms of its diameter (which is more common) assuming spherical shape. For the number of magnetic ions taken above the diameters of the particles will be 49, 62, 90, 106 and 118 Å respectively which cover the usual range of ultra-fine particles.

11. Discussion

Several approximations have been made in the derivation of the final expression for $1/\tau_{sp}$ and the calculation of its values as a function of temperature and therefore it may not be wise to make claims for its precision given the wide range of magnetic particles. Still the calculated relaxation rates could be acceptable well within one order of magnitude. These are particularly encouraging in the context of the Mossbabuer studies of ultra-fine particles. The calculated values indicate that Mossbauer spectra could show the effect of magnetic relaxation

Table 1. Relaxation rates have been calculated for $J' = 2.12 \times 10^{-6}$ erg cm^{-1}, $\theta_D = 700$ K, $\theta_C = 900$ K, $S = 2.5$ and $K = 10^5$ erg cm^{-3} and the number of magnetic ions N has been shown at the top of each column. The parameter R_0 does not depend on N and its variation with temperature has been shown. The particle size indicates the diameter of the particle, assumed to be of spherical shape (10 Å = 1 nm).

T (K)	R_0 (s^{-1})	$1/\tau_{sp}$ (s^{-1})				
		$N = 500$	1000	3000	5000	7000
10	1.1×10^9	1.2×1^7	1.4×10^5	1.8×10^{-3}	2.6×10^{-11}	3.6×10^{-19}
20	5.8×10^{10}	6.1×10^9	6.3×10^8	7.4×10^4	7.9×10^0	1.0×10^{-3}
30	2.8×10^{11}	6.2×10^{10}	1.4×10^{10}	3.3×10^7	7.9×10^4	1.9×10^2
40	7.0×10^{11}	2.2×10^{11}	7.3×10^{10}	7.8×10^8	8.5×10^6	9.2×10^4
50	1.3×10^{12}	5.2×10^{11}	2.1×10^{11}	5.7×10^9	1.5×10^8	4.1×10^6
60	2.1×10^{12}	9.8×10^{11}	4.6×10^{11}	2.2×10^{10}	1.1×10^9	5.4×10^7
70	3.0×10^{12}	1.6×10^{12}	8.3×10^{11}	6.2×10^{10}	4.7×10^9	3.5×10^8
80	4.1×10^{12}	2.3×10^{12}	1.3×10^{12}	1.4×10^{11}	1.4×10^{10}	1.5×10^9
90	5.3×10^{12}	3.2×10^{12}	1.9×10^{12}	2.6×10^{11}	3.5×10^{10}	4.6×10^9
100	6.6×10^{12}	4.2×10^{12}	2.6×10^{12}	4.4×10^{11}	7.2×10^{10}	1.2×10^{10}
Particle size (Å) =		49	62	90	106	118

on small particles of dimension $\sim$100 Å at liquid nitrogen or lower temperatures when $1/\tau_{sp}$ is comparable to the Mossbauer timescale of 10^7–10^9 s^{-1} [28, 29]. This is generally in agreement with the experiments on the systems described. The smaller size particles require much lower temperatures for similar observations. For example, a particle of size 49 Å may show a magnetic spectrum below 20 K but a particle of size 106 Å may show a magnetic spectrum up to 50 K which extends up to 70 K for a particle of size 118 Å, etc. The model presented here provides a credible quantum mechanical microscopic framework for the superparamagnetic relaxation process in terms of exchange of energy between magnons and phonons within a magnetic crystal, particularly at low temperatures when $T \ll \theta_D$ and θ_C. The present work is expected to supplement the study of nano-particles through other physical techniques in general.

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