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ELECTRON SPIN-LATTICE RELAXATION IN FRACTALS *

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ABSTRACT

We have developed the theory of the spin-fracton interaction for paramagnetic ions in fractal structures. The interaction is exponentially damped by the self-similarity length of the fractal and by the range dimensionality d_ϕ . The relaxation time of the spin due to the absorption and emission of the fracton has been calculated for a general dimensionality called the Raman dimensionality d_R , which for the fractons differs from the Hausdorff (fractal) dimensionality, D , as well as from the Euclidean dimensionality, d . The exponent of the energy level separation in the relaxation rate varies with $d_R d_\phi / D$. We have calculated the spin relaxation rate due to a new type of Raman process in which one fracton is absorbed to affect a spin transition from one electronic level to another and later another fracton is emitted along with a spin transition such that the difference in the energies of the two fractons is equal to the electronic energy level separation. The temperature and the dimensionality dependence of such a process has been found in several approximations. In one of the approximations where the van Vleck relaxation rate for a spin in a crystal is known to vary with temperature as T^9 , our calculated variation for fractals turns out to be $T^{6.6}$, whereas the experimental value for Fe^{3+} in frozen solutions of myoglobin azide is $T^{6.3}$. Since we used $d_R = 4/3$ and the fracton range dimensionality $d_\phi = D/1.8$, we expect to measure the dimensionalities of the problem by measuring the temperature dependence of the relaxation times. We have also calculated the shift of the paramagnetic resonance transition for a spin in a fractal for general dimensionalities.

1. Introduction

Mørup and Knudsen [1] have found that the width of the Mössbauer line can be explained from the theory of spin-lattice relaxation. A long time ago, van Vleck [2] developed the theory of spin-lattice relaxation for paramagnetic ions in insulating crystals. According to this theory, the relaxation rate varies with temperature as $1/T_1 \simeq T$ for the one-phonon process and T^7 for the two-phonon Raman process for non-Kramers ions and T^9 for Kramers ions. An exponential dependence is also found [3]. We have found important modifications of van Vleck's results [3]. Instead of taking the difference of the frequencies of the two phonons as equal to the electronic energy level separation, we can take the sum [4,5] in which case at low temperatures, the sum process varies as $1/T_1 \propto \exp(-\Delta/T)$ and at high temperatures it gives $1/T_1 \propto T^2$ and for intermediate temperatures only a numerical solution [6] is possible which peaks at a temperature of $\Delta/7$ where Δ is the electronic energy level separation. In some cases, more than one type of magnetic atom is present in the lattice so that cross relaxation occurs [7] and the temperature dependence is altered from the van Vleck's value [8] whereas in other cases a multiphonon process may be operative [9]. In the case of semiconducting lattices the problem is altogether different [10] as we expect to find the phonon-induced Auger process or the radiative process [11].

These days there is considerable interest in the study of naturally grown materials, such as proteins, sponges, resins and glues which may be represented by fractals [12]. These materials grow in a selfsimilar manner until a critical length is reached. One of the

recent examples [13, 14] is that of growth of oil into glycerine in etched-glass networks where fingers [15] form a chaotic structure with a fractal dimension, $D = 1.72$. It is found [16] that the Hausdorff [17] dimensionality D is less than the Euclidean dimensionality d ($D=5/3$ for $d=2$). On a self-similar fractal structure the number of points inside a circle of radius r which is a measure of mass and the radius itself is a power law with noninteger exponent, i.e., $N(r) \propto r^D$ so that D may be evaluated from $N(r)$. In the case of a dielectric breakdown Niemeyer et al [18] have found $D=1.7$ for $d=2$.

Recently, Stapleton et al [19] have studied the relaxation time of Fe^{3+} in three haemoproteins, myoglobin azide, ferricytochrome C and cytochrome P-450 from *Pseudomonas putida*. In all the cases, the results may be explained from a dimensionality less than three. The suggestion of Stapleton et al is that an effective dimensionality of $D=1.65 \pm 0.04$ should be used to obtain agreement between van Vleck processes and the experimental data. This effective value corresponds to the fractal (Hausdorff) dimensionality of $D=5/3$ for $d=2$ for self-avoiding random walk. Shrivastava [20] performed the calculation of one-fracton and two-fracton scattering processes from the paramagnetic ions in fractals for the first time from a hamiltonian approach which give rise to the correct spin-fracton relaxation times. In a recent publication [21] we have calculated the recoil-free fraction of the nuclear γ -radiation from a fractal. In this paper, we develop the theory of spin relaxation of paramagnetic ions in fractal systems for general dimensionalities which are not necessarily Euclidean. We also calculate the shift of the frequency of the paramagnetic resonance as a result of the spin-fracton interaction. We define a good quantum-mechanical interaction of spin with fractons which are the vibrational excitations in a fractal or the fractal analogues of phonons in crystals and calculate the spin relaxation time for one

and two fracton processes. It is our hope that our theory will be of use to study the paramagnetic resonance and relaxation of paramagnetic ions in proteins and other self-similar materials, with special application to Mössbauer spectra of proteins and complement our previous study [21] of the recoilless fraction.

2. The spin-fracton interaction

We write the unperturbed Hamiltonian for spin and fractons as,

$$\mathcal{H}_0 = \Omega S_z + \sum_{\mathbf{k}} \hbar \omega_{\mathbf{k}} a_{\mathbf{k}}^\dagger a_{\mathbf{k}} \quad (2.1)$$

where Ω is the frequency of the spin and $\omega_{\mathbf{k}}$ is that of fractons.

The operators $a_{\mathbf{k}}^\dagger$ and $a_{\mathbf{k}}$ create and destroy fractons. The interaction is written as,

$$\mathcal{H}' = \sum_{\mathbf{k}, \alpha} \sum_{n,m} V_n^m \left(\frac{\hbar}{2M\omega_{\mathbf{k}}} \right)^{q/2} |k|^q (a_{\mathbf{k},\alpha}^\dagger + a_{\mathbf{k},\alpha}) \phi_{\mathbf{k},\alpha}(\omega_{\mathbf{k}}, \alpha) \quad (2.2)$$

where V_n^m are the energy operators which change the state of the paramagnetic ion, M is the mass of the fractal, \vec{k} the wave vector of fractons with a suitable wave damping factor, $\phi_{\mathbf{k},\alpha}(\omega_{\mathbf{k}}, \alpha)$ in dimensionality,

$$q = d_R d_\phi D^{-1} \quad (2.3)$$

where d_ϕ is the value of the dimensionality associated with the range, first discussed by Shrivastava [22] in the case of crystal fields and in this case for fractons, D is the fractal (Hausdorff) dimensionality determined by counting mass units as a function of radius vector, and d_R is the Raman dimensionality experienced by the fractons which are the vibrational excitations of the fractal of which Cayley tree is an example [23]. The eigen values of the fracton creation and annihilation operators are damped by

$$\phi_{\mathbf{k},\alpha}(\omega_{\mathbf{k}}, \alpha) = \left(\frac{l_{\omega_{\mathbf{k}}}}{L} \right)^{D/2} \exp \left[-\frac{1}{2} \left(\frac{l}{l_{\omega_{\mathbf{k}}}} \right)^{d_\phi} \right] \quad (2.4)$$

where $l_{\omega_{\mathbf{k}}}$ is the localisation length as a function of frequency in the α th mode of vibration given by

$$l_{\omega_{\mathbf{k}}} = a \left(\omega_{\mathbf{k}} / \omega_{FD} \right)^{-d_R/D} \quad (2.5)$$

where a is an atomic length and ω_{FD} is the cutoff frequency for the fractons, related to the Debye frequency ω_D by

$$\omega_{FD} = \omega_D (1/a)^\theta \quad (2.6)$$

where θ is the diffusion exponent in the diffusion of mass as a function of distance, $D(r) \propto r^{-\theta}$.

3. The direct process

We imagine a two level spin system in a fractal. The lower level is designated $|a\rangle$ and the upper $|b\rangle$ with the energy separation $E_b - E_a = \Delta$.

The probability of absorption of a fracton along with the electronic transition from $|a\rangle$ to $|b\rangle$ is given by,

$$P_{b \leftarrow a} = \frac{2\pi}{\hbar} \left| \langle b, n_{\mathbf{k}} - 1 | \mathcal{H}' | a, n_{\mathbf{k}} \rangle \right|^2 \delta(E_f - E_i) \quad (3.1)$$

The energy of the initial state is given by $E_i = E_a + n_{\mathbf{k}} \hbar \omega_{\mathbf{k}}$

and that the final state is $E_f = E_b + (n_{\mathbf{k}} - 1) \hbar \omega_{\mathbf{k}}$. The argument

of the δ -function, $\Delta - \hbar \omega_{\mathbf{k}}$, ensures the conservation of energy. Upon substituting the second term of the interaction from (2.2) to (3.1)

we find

$$P_{b \leftarrow a} = \frac{2\pi}{\hbar} \sum_{\mathbf{k}} \left| \langle b | \sum_{n,m} V_n^m | a \rangle \right|^2 \left(\frac{\hbar}{2M\omega_{\mathbf{k}}} \right)^q |k|^{2q} n_{\mathbf{k}} \phi_{\mathbf{k}}^2 \delta(\Delta - \hbar \omega_{\mathbf{k}}) \quad (3.2)$$

The maximum length of the fractal is given by L' so that the summation in (3.2) may be changed to integration by making the replacement,

$$\sum_k = \int 4\pi \left(\frac{L'}{2\pi} \right)^3 |k|^{d-1} dk \quad (3.3)$$

We define the mass density $M/L' = \rho$ so that upon substituting (3.3) into (3.2) we find,

$$P_{b \leftarrow a} = C_1 \int \omega_k^{-q} |k|^{3q-1} n_k \phi_k^2 \delta(\Delta - \hbar\omega) dk \quad (3.4)$$

where

$$C_1 = \frac{24\pi^2}{\hbar} \left| \langle b | \sum_{n,m} v_{n,m}^a | a \rangle \right|^2 \left(\frac{\hbar}{4\rho\pi} \right)^q \quad (3.5)$$

We change the wave vector into frequency to evaluate the G -function by use of linear dispersion, $\omega = v|k|$ where v is the sound velocity in the fractal, so that we find the probability of absorption of a fracton by the spin as,

$$P_{b \leftarrow a} = \frac{C_1}{\hbar v^{3q}} \int \omega^{2q-1} n_\omega \phi_\omega^2 \delta\left(\frac{\Delta}{\hbar} - \omega\right) d\omega \quad (3.6)$$

Evaluating the δ -function and defining the Bose factor at the energy

Δ and the range factor ϕ we find,

$$P_{b \leftarrow a} = \frac{C_1}{\hbar v^{3q}} \left(\frac{\Delta}{\hbar} \right)^{2q-1} n_A \phi_A^2 \quad (3.7)$$

Similarly, we calculate the probability of emission of a fracton by the spin in undergoing a transition from $|b\rangle$ to $|a\rangle$ to be

$$P_{a \leftarrow b} = \frac{C_1}{\hbar v^{3q}} \left(\frac{\Delta}{\hbar} \right)^{2q-1} (n_A + 1) \phi_A^2 \quad (3.8)$$

so that the spin relaxation rate using the relation $1/T_1 = P_{a \leftarrow b} + P_{b \leftarrow a}$ is found to be,

$$1/T_1 = \frac{C_1}{\hbar v^{3q}} \left(\frac{\Delta}{\hbar} \right)^{2q-1} \phi_A^2 \coth \frac{\Delta}{2k_B T} \quad (3.9)$$

Using (2.4) and (2.5) we find the range factor at resonance to be

$$\phi_A^2 = \left(\frac{L}{a} \right)^D \left(\frac{\Delta}{\hbar \omega_{TD}} \right)^{d_R} \exp \left[- \left(\frac{L}{\ell} \right)^{d_\phi} \right] \quad (3.10)$$

which when substituted in (3.9) gives,

$$1/T_1 = \frac{C_1}{\hbar v^{3q}} \left(\frac{\Delta}{\hbar} \right)^{2q-1+d_R} \left(\frac{L}{a} \right)^D \left(\frac{\hbar \omega_{TD}}{\hbar} \right)^{-d_R} \exp \left[- \left(\frac{L}{\ell} \right)^{d_\phi} \right] \coth \frac{\Delta}{2k_B T} \quad (3.11)$$

At low temperatures $\coth(\Delta/2k_B T) \approx 2k_B T/\Delta$ so that the temperature and energy dependence occurs in the form

$$1/T_1 \propto T \Delta^{2q-2+d_R} \quad (3.12)$$

Since for two levels in a magnetic field the energy level separation

is $g\mu_B H$, the dependence on field in (3.12) is of the form,

$$1/T_1 \propto T H^{2q-2+d_R} \quad (3.13)$$

For $q=d_R$, d_ϕ/D , $d=3$, $d_R=4/3$, $D=5/2$, $d_\phi=1/1.8$ as given by Kapitulin and Deutscher [24] we find that $2q-2+d_R=0.81$ so that a magnetic field dependence of $H^{0.81}$ is predicted. Alexander et al [25] wrote down some results semiquantitatively with constants of proportionalities left out. We are the first [20,26] to find a proper quantum mechanical definition of the spin-lattice relaxation rate of paramagnetic ions in fractals.

4. The Raman process in Euclidean dimensionality, d .

We consider the Raman process in a three level system, $|a\rangle$, $|b\rangle$ and $|c\rangle$ in the ascending order of energy. The absorption of a phonon accompanied by the spin transition from $|a\rangle$ to $|c\rangle$ and then emission of another phonon accompanied by the spin transition from $|c\rangle$ to $|b\rangle$ such that the difference in the frequencies of the two phonons is equal to the electronic energy level separation, $E_b - E_a$, gives rise to a finite relaxation time. To calculate this process in the general dimensionality in

Euclidean space, we write the interaction as

$$H' = \sum_{k,\alpha} \sum_{n,m} v_n \left(\frac{\hbar}{2m\omega_k} \right)^{1/2} |k| (a_{k,\alpha}^\dagger + a_{k,\alpha}) \quad (4.1)$$

The probability of absorption of a phonon and the spin transition from $|a\rangle$ to $|c\rangle$ and in a second step emission of a phonon and the spin transition from $|c\rangle$ to $|b\rangle$ is given by

$$P_{bca} = \frac{2\pi}{\hbar} \left| \frac{\langle b, n_k, +1, n_k-1 | H' | n_k, n_k-1, c \rangle \langle c, n_k, n_k-1 | H' | n_k, n_k, a \rangle}{E_c - E_a - \hbar\omega_k} \right|^2 \quad (4.2)$$

Evaluating the matrix elements and changing the summation into integration we find that,

$$P_{bca} = \frac{2\pi}{\hbar} \left| \frac{\langle b | \sum_{n,m} v_n | c \rangle \langle c | \sum_{n,m} v_n | a \rangle}{E_c - E_a - \hbar\omega_k} \right|^2 n_k(n_k+1) \left(\frac{\hbar}{2\rho} \right)^2 \frac{k^2 \omega_k^2}{\omega_k \omega_k} \delta\left(\frac{\Delta}{\hbar} + \omega_k, -\omega_k\right) \left(\frac{12\pi L^d}{(2\pi)^d} \right)^2 k^{d-1} dk \quad (4.3)$$

where d is the Euclidean dimensionality and L is the length of the sample. We solve the above integral in a few special cases.

Case I. We take the case of two closely separated levels with one more level far apart from the lower two, so that, $E_b - E_a \ll \hbar\omega_k$, and $E_c - E_a \gg \hbar\omega_k$. The expression (4.3) upon using the relation $\omega = \Theta k$ becomes,

$$P_{bca} = \frac{C_2}{\hbar} \int \int n_k(n_k+1) \frac{\omega^d \omega'^d}{v^{2d+4}} \frac{d\omega d\omega'}{\Delta^2} \delta\left(\frac{\Delta}{\hbar} + \omega' - \omega\right) \quad (4.4)$$

where

$$C_2 = \frac{2\pi}{\hbar} \left| \langle b | \sum_{n,m} v_n | c \rangle \langle c | \sum_{n,m} v_n | a \rangle \right|^2 \frac{36 \pi^2 \hbar^2}{(2\pi)^{2d} \rho^2} \quad (4.5)$$

for $\omega' + \Delta \approx \omega$, upon evaluating the δ -function the above probability becomes,

$$P_{bca} = \frac{C_2}{\Delta^2 \hbar^3 v^{2d+4}} \int_0^{\omega_D} n_\omega (n_\omega + 1) \omega^{2d} d\omega \quad (4.6)$$

Upon making the change of variables, $\hbar\omega/k_B T = x$, the above integral

$$1/T_1 = \frac{2C_2}{\Delta^2 \hbar^3 v^{2d+4}} \left(\frac{k_B T}{\hbar} \right)^{2d+1} \int n_x (n_x + 1) x^{2d} dx \quad (4.7)$$

gives the relaxation rate of which for a three dimensional solid, $d=3$, varies as T^7 .

Case II. In the case of closely spaced levels, the energy denominator in (4.3) may be written as $(E_c - E_a - \hbar\omega_k)^2 \approx (\hbar\omega_k)^2$ so that two powers of frequency are reduced. The probability (4.3) then becomes,

$$P_{bca} = \frac{C_2}{\hbar} \int \int n(n'+1) \omega^{d-2} \omega'^d d\omega d\omega' \delta\left(\frac{\Delta}{\hbar} + \omega' - \omega\right) \quad (4.8)$$

For $\Delta \ll \omega$, the relaxation rate in this case varies as T^{2d-1} or T^5 for $d=3$.

Case III. In the case of Kramers ions [3] the matrix element in (4.3) involves the time reversed states so that the relaxation rate varies as T^{2d+3} or T^9 for $d=3$. There are many other interesting cases of the Raman process which were discussed earlier [27].

Case IV. At high temperatures, the number density dependent factor in the integrand of (4.6) may be written as

$$\frac{e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2} \approx \left(\frac{k_B T}{\hbar\omega} \right)^2 \quad (4.9)$$

so that the probability (4.6) becomes,

$$P_{bca} = \frac{C_2}{\Delta^2 \hbar^3 v^{2d+4}} \int_0^{\omega_D} (k_B T)^2 \omega^{2d-2} d\omega \quad (4.10)$$

which upon complete integration gives the spin-lattice relaxation rate for general dimensionality as,

$$1/T_1 = \frac{2C_2 (k_B T)^2 \omega_D^{2d-1}}{\Delta^2 \hbar^3 v^{2d+4} (2d-1)} \quad (4.11)$$

in which the temperature dependence of T^2 is independent of the dimensionality, d . However, the coefficient does depend on d .

5. The Raman process in fractal dimensionality

In the case of fractional dimensionality, the expression for the Raman probability (4.2) remains unchanged, except that we use the interaction (2.2) along with its prescriptions given by (2.4) to (2.6). The probability (4.2) is now found to be,

$$P_{\text{boa}} = C_3 \frac{n_{k,\alpha} (n_{k',\alpha} + 1) \phi_{k,\alpha}^2 \phi_{k',\alpha}^2 |k|^{3q-1} |k'|^{3q-1}}{|\Delta_0 - \hbar\omega_k|^2 \omega_k^q \omega_{k'}^q} \delta(A + \hbar\omega_k - \hbar\omega_{k'}) dk dk' \quad (5.1)$$

where

$$C_3 = \frac{18\pi}{\hbar} \left| \langle b | \sum_{n,m} v_n^m | \phi \rangle \langle c | \sum_{n,m} v_n^m | a \rangle \right|^2 \left(\frac{\hbar}{2\rho} \right)^{2q} (4\pi)^{2-2q} \quad (5.2)$$

We solve (5.1) in several approximations.

Approximation I: We take the case of $\Delta_0 \gg \hbar\omega_k$ while $\Delta \ll \hbar\omega_k$ so that in the denominator of (5.1), we ignore the fracton frequency.

The probability then becomes,

$$P_{\text{boa}} = \frac{C_3}{\hbar \Delta_0^2 v^{6q}} \int n_{\omega'} (n_{\omega'} + 1) \phi_{\omega'}^4 \omega'^{4q-2} d\omega' \quad (5.3)$$

which upon making the change of variables $\hbar\omega/k_B T = x$, becomes

$$P_{\text{boa}} = \frac{C_3}{\hbar \Delta_0^2 v^{6q}} \left(\frac{k_B T}{\hbar} \right)^{4q-1} \int n_x (n_x + 1) \phi_x^4 x^{4q-2} dx \quad (5.4)$$

The range factor

$$\phi_{\omega}^4 = \left(\frac{\ell\omega}{L} \right)^{-2D} \exp \left[-2 \left(\frac{L}{\ell\omega_x} \right)^{d\phi} \right] \quad (5.5)$$

upon using (2.5) becomes,

$$\phi_{\omega}^4 = \left(\frac{\ell}{L} \right)^{-2D} \left(\frac{\omega}{\omega_0} \right)^{2d_R} \exp \left[-2 \left(\frac{L}{\ell\omega_x} \right)^{d\phi} \right] \quad (5.6)$$

which upon substituting in (5.4) gives,

$$P_{\text{boa}} = \frac{C_3}{\hbar \Delta_0^2 v^{6q}} \left(\frac{k_B T}{\hbar} \right)^{4q-1+2d_R} \int n_x (n_x + 1) x^{4q-2+2d_R} \left(\frac{\ell}{L} \right)^{-2D} \omega_x^{-2d_R} \times \exp \left[-2 \left(\frac{L}{\ell x} \right)^{d\phi} \right] dx \quad (5.7)$$

The relaxation rate due to the above processes varies with temperature as $T^{4q-1+2d_R}$. Since $q = d_R d_\phi / D$, and $d_R = 4/3$, $D = 5/2$ and $d_\phi \approx D/1.8$ for $d=3$, the exponent of temperature is found to be $4q-1+2d_R = 4.63$ in the case of fractals whereas an exponent of 7 would result in the case of three-dimensional crystals as discussed below (4.7).

Approximation II. In the case of $\hbar\omega_k \gg \Delta_0$ and $\Delta \ll \hbar\omega_k$ we ignore the electronic energy in the denominator of (5.1) so that we obtain,

$$P_{\text{boa}} = \frac{C_3}{\hbar^3} \frac{n_{k,\alpha} (n_{k',\alpha} + 1) \phi_{k,\alpha}^2 \phi_{k',\alpha}^2 |k|^{3q-1} |k'|^{3q-1} \delta(\frac{A}{\hbar} + \omega_k - \omega_{k'}) dk dk'}{\omega^{q+2} \omega'^q} \quad (5.8)$$

which in the approximation $\Delta + \hbar\omega_k \approx \hbar\omega_{k'}$, becomes,

$$P_{\text{boa}} = \frac{C_3}{\hbar v^{6q}} \left(\frac{k_B T}{\hbar} \right)^{4q-3} \int n_x (n_x + 1) \phi_x^4 x^{4q-4} dx \quad (5.9)$$

Upon evaluating the range factor in the integral we find that

$$1/T_1 = \frac{2C_3}{\hbar v^{6q}} \left(\frac{k_B T}{\hbar} \right)^{4q-3+2d_R} \left(\frac{L}{\ell} \right)^{2D} \int \omega^{-2d_R} \exp \left[-2 \left(\frac{L}{\ell x} \right)^{d\phi} \right] \times n_x (n_x + 1) x^{4q-4+2d_R} dx \quad (5.10)$$

the temperature dependence in which is of the form $T^{4q-3+2d_R}$

at low temperatures which for $d=3$ gives $T^{2.63}$ for the same values of

fractal dimensionalities as given below eq.(5.7).

Approximation III: In the case of Kramers time reversed states, there are always two intermediate states. Therefore the matrix element which occurs in the Raman process is,

$$\begin{aligned} & \langle -\frac{1}{2} a | \sum_{n,m} v_n^m | \frac{1}{2} o \rangle \langle \frac{1}{2} o | \sum_{n,m} v_n^m | \frac{1}{2} a \rangle \left\{ \frac{1}{\hbar\omega - \Delta_0} + \frac{1}{\hbar\omega + \Delta_0} \right\} \\ & = \langle -\frac{1}{2} a | \sum_{n,m} v_n^m | \frac{1}{2} o \rangle \langle \frac{1}{2} o | \sum_{n,m} v_n^m | \frac{1}{2} a \rangle \left\{ \frac{2\hbar\omega}{(\hbar\omega)^2 - \Delta_0^2} \right\} \end{aligned} \quad (5.11)$$

The Raman probability now becomes,

$$P_{\text{Raman}} = \frac{C_4}{\hbar \Delta_0^4 v^{6q}} \int n_x(n_x+1) \phi_\omega^4 \omega^{4q} d\omega \quad (5.12)$$

where

$$C_4 = 1152 \Delta \pi^3 \left(\frac{\hbar}{4\rho R} \right)^{2q} \left| \langle -\frac{1}{2} a | \sum_{n,m} v_n^m | \frac{1}{2} o \rangle \langle \frac{1}{2} o | \sum_{n,m} v_n^m | \frac{1}{2} a \rangle \right|^2 \quad (5.13)$$

so that the relaxation rate in the case of Kramers ions in fractals is found to be,

$$1/\tau_1 = \frac{2C_4}{\hbar \Delta_0^4 v^{6q}} \left(\frac{k_B T}{\hbar} \right)^{4q+1+2d_R} \int n(n+1) x^{4q+2d_R} \left(\frac{L}{a} \right)^{2D} \omega_{FD}^{-2d_R} \exp \left[-2 \left(\frac{L}{\ell_x} \right)^d \right] \quad (5.14)$$

which at low temperatures has a temperature dependence of $T^{4q+1+2d_R}$. For $d=3$ and other values as given below (5.7) it is found to be $T^{6.63}$, to be compared with the experimental value [19] of $T^{6.3}$ for Fe^{3+} in myoglobin aside frozen solutions. In view of the uncertainties in the values of various dimensionalities our calculated value may be thought to be in reasonable agreement with the experimental value.

6. The frequency shift of a spin in a fractal

We calculate the dynamical energy shift of a paramagnetic ion in a fractal. This energy decreases exponentially at large distances with an exponent of the range dimensionality and hence on the fractal (Hausdorff) dimensionality. The temperature dependence of this energy involves the fracton Raman dimensionality, d_R in addition to the fractal dimensionality, D . We consider the transition of the spin from the state $|a\rangle$ to the state $|b\rangle$ by absorption of a fracton and in a second step the emission of a fracton along with the spin transition from $|b\rangle$ to $|a\rangle$ so that $|a\rangle$ acquires the energy shift which is calculated to be,

$$\begin{aligned} \delta E_a = & 6(2\pi)^{1-q} \langle a | \sum_{n,m} v_n^m | b \rangle \langle b | \sum_{n,m} v_n^m | a \rangle |k|^{3q-1} \phi_{k,\alpha}^2 \left(\frac{\hbar}{2\rho \omega_{k,\alpha}} \right)^q \\ & \left(\frac{n_{k,\alpha} + 1}{\Delta + \hbar\omega_{k,\alpha}} + \frac{n_{k,\alpha}}{\Delta - \hbar\omega_{k,\alpha}} \right) dk \end{aligned} \quad (6.1)$$

which we integrate from the smallest fracton frequency $\omega(R_0)$ for a cluster of radius R_0 to the maximum fracton frequency, ω_{FD} . Usually the electronic energies are larger than the fracton energies, $\Delta \gg \hbar\omega_{k,\alpha}$ so that (6.1) becomes,

$$\delta E_a = \frac{C_5}{\Delta} \int \frac{|k|^{3q-1} \phi_{k,\alpha}^2 (2n_{k,\alpha} + 1) dk}{\omega_{k,\alpha}^q} \quad (6.2)$$

where

$$C_5 = 3 \langle a | \sum_{n,m} v_n^m | b \rangle \langle b | \sum_{n,m} v_n^m | a \rangle (4\pi)^{1-q} (\hbar/\rho)^q \quad (6.3)$$

Using linear dispersion $\omega = v|k|$, and making the change of variables, $\hbar\omega/k_B T = x$, we find that (6.2) reduces to,

$$\delta E_n = \frac{C_5}{\Delta \nu^{3q}} \left(\frac{k_B T}{\hbar} \right)^{2q} \int_{x(R_0)}^{x_{FD}} (2n+1) x^{2q-1} \phi_x^2 dx \quad (6.4)$$

where the square of the range factor is given by

$$\phi_x^2 = \left(\frac{x}{L} \right)^{-D} \omega_{FD}^{-d_R/D} \left(\frac{k_B T}{\hbar} \right)^{d_R} x^{d_R} \exp \left[-\frac{1}{2} \left(\frac{L}{x} \right)^{d_\phi} \right] \quad (6.5)$$

with

$$\hat{k}_x = a \omega_{FD}^{d_R/D} \left(\frac{k_B T x}{\hbar} \right)^{-d_R/D} \quad (6.6)$$

Therefore this energy shift varies as $T^{2q + d_R} \exp(-C_x T^{d_\phi})$ where,

$$C_x = \frac{1}{2} \frac{L^{d_\phi} \omega_{FD}^{-d}}{a^{d_\phi}} \left(\frac{k_B T}{\hbar} \right)^q \quad (6.7)$$

We see from (6.5) that the energy decreases exponentially as L^{d_ϕ} which means that the effect is localized near the spin. It is found that $D=1.8$ d_ϕ so that $q = d_R/1.8$. Therefore the preexponential factor in (6.5) is of the form of $T^{2.1d_R}$ or $T^{2.98}$ for $d=3$, $d_R=1.42$ for a fractal, whereas T^4 was found for the case of a spin interacting with phonons in crystals [28,29]. The energy (6.4) is large enough to be measured and is well established in the analogous case of phonons. In the limit of Euclidean dimensionality $d = \infty$, the fracton Raman dimensionality d_R is $4/3$ so that the preexponential factor varies as $T^{2.8}$. However, the value of q in the argument of the exponential in (6.4) is 0.78 for $d=3$, $d_R=1.42$ and 0.74 for $d=\infty$, $d_R=4/3$. In this way we see that there is a Jahn-Teller like effect in fractals containing paramagnetic ions. Stapleton et al [19] measured the temperature dependence of the spin relaxation time of iron in several proteins from which they found that the van Vleck processes were not obeyed unless the vibrational density of states came from the fractal structure of the proteins with dimensionality D which measures the mass distribution. It is now believed that the fracton Raman dimensionality d_R

should be used rather than the fractal dimensionality D . The effect discussed in the present work shows up in terms of the shift of the electron spin resonance line as a function of temperature. The line shift measurements when they become available may make it possible to measure the dimensionality d_R which is experienced by fractons in fractals.

7. Conclusions

We have reinvestigated the problem of spin-lattice relaxation for general dimensionality in the usual Euclidean sense. The spin-phonon interaction of crystals is reformulated for the spin-fracton interaction in fractals. In these systems, the fractal or Hausdorff dimensionality is less than the Euclidean value. Besides, the fractons do not follow the same dimensionality as fractals do. Therefore, the fractal as well as the fracton Raman dimensionalities associated with vibrations are treated as distinct from each other. The complete theory of spin-lattice relaxation is thus reformulated. We have performed the calculation of the relaxation time for the direct one-fracton process as well as for the two-fracton Raman process. We have also calculated the shift of the spin resonance line due to the spin-fracton interaction. We believe that our results will be useful for the interpretation of widths of the Mössbauer lines in proteins and like materials.

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