Relaxation time of the nanomagnet Fe₄.

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Abstract

The magnetic behaviour of the molecular nanomagnet Fe₄ is very well simulated by a single spin model Hamiltonian in a crystal field with $S = 5$. The crystal field parameters were determined from the inelastic neutron scattering (INS) spectra. Here we show that the quantum effects are crucial to understand the saturation of the relaxation time observed at very low temperature at variance with the standard master equation result that leads to an Arrhenius law at any temperature. Very deep downward spikes in correspondence of the anticrossing fields are found in the relaxation time vs field at low temperature. We compare our results with those obtained by previous approaches worked out to fit experimental data on Mn₁₂.

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I. INTRODUCTION

An expanding area of the magnetism concerns the single molecule magnets (SMMs)\(^1\) with slow relaxation of the magnetization at low temperature.

Many interesting basic properties as magnetic quantum tunneling (MQT) as well as possible technical application in quantum computing or magnetic storage make the SMMs particularly attractive.

We focus on the tetrairon cluster \(\text{Fe}_4(\text{thme})_2(\text{dpm})_6\) (briefly \(\text{Fe}_4\))\(^2\) where thme indicates the triply deprotonated 1,1,1-tris(hydroxylmethyl)ethane \(\text{H}_3\text{thme}\) and dpm indicates the deprotonated dipivaloylmethane \(\text{Hdpm}\). The complete chemical formula of the tetrairon cluster reads \(\text{C}_{76}\text{H}_{132}\text{O}_{18}\text{Fe}_4\).

The tetrairon cluster \(\text{Fe}_4\) is a puzzle for theoretical physicists because the fit with experimental data of inelastic neutron scattering (INS)\(^3\) implies the existence of a term in the crystal field Hamiltonian that violates the \(D_3\) symmetry of the molecule as deduced by a single-crystal X-ray study\(^2\) performed at \(T = 100\) K. The existence of such a symmetry-violating term may be ascribed to two different sources:

i) the X-ray study at \(T = 100\) K established that the \(\text{Fe}_4\) ions of the iron cluster are placed on the vertices and at the centre of an equilateral triangle (\(D_3\) symmetry); however, a small distortion of the equilateral to isosceles triangle, as suggested by Carretta et al.\(^3\), could violate the \(D_3\) symmetry. Rastelli and Tassi\(^4\) proved that a distortion of less than half degree away from the equilateral symmetry is able to recover the term used in the fit with INS experiment. The distortion could be ascribed to a true distortion of the tetrairon cluster occurring at low temperature or the tolerance of the single-crystal X-ray study or the use of a powder sample in INS experiment.

ii) If all the sources of possible distortion have to be excluded some not yet identified microscopic mechanism like second-order Dzyaloshinskii-Moriya (DM) effects\(^5\) might yield an effective term similar to that used by Carretta et al.\(^3\) to fit INS data.

Experimental data in zero field\(^2\) show that the relaxation time of magnetization of the tetrairon cluster \(\text{Fe}_4\) shows an Arrhenius law for temperature \(T \gtrsim 1\) K while saturation is found for \(T \lesssim 0.2\) K, where thermal activation is negligible and quantum effects are dominant.

The theoretical approach to the relaxation time of the magnetization of a SMM is based
on the master equation\textsuperscript{6} in which the transition probability rates between the magnetic states are related to the spin-phonon interaction. For temperature high enough only thermal activation is accounted for\textsuperscript{7} neglecting quantum tunneling. This approach leads to the Arrhenius law for the relaxation time vs temperature in good agreement with the experiment\textsuperscript{8} on Mn\textsubscript{12}. On the contrary in the very low temperature regime quantum effects are dominant, so that the relaxation time was evaluated by the Fermi’s golden rule at zero temperature\textsuperscript{9} and the order of magnitude of the relaxation time of Mn\textsubscript{12} in weak external magnetic field was recovered.

Then a generalized master equation\textsuperscript{10} was proposed in order to account for the quantum tunneling at finite temperature. However, an approximation on the time dependence of the off-diagonal elements of the density matrix to reduce drastically the number of differential equations, restricts the result to temperatures high enough. This calculation gave a satisfactory fitting of the experimental data on Mn\textsubscript{12} between $T = 1.9$ and $2.8$ K explaining the deep downward spikes of the relaxation time as function of the external magnetic field in correspondence to the fields at which the energy levels of the diagonal part of the crystal field Hamiltonian cross each other. In this way the enhanced relaxation rate was correlated to the quantum tunneling in presence of spin-phonon interaction.

Until now an approach to describe the crossover from the pure quantum behaviour in the low temperature regime to the thermal activated regime, does not exist. We propose a new generalized master equation (GME) suitable to describe both the quantum and the thermal activated regime at any temperature and we use this approach to describe the relaxation time of the tetrairon cluster Fe\textsubscript{4}. We have numerically diagonalized the crystal field Hamiltonian in an external magnetic field and we have accounted for the temperature dependent transition probability rates by the Fermi’s golden rule. The master equation we propose makes use of the main contributions to quantum tunneling selected by looking at the zero temperature rigorous result.

We have also applied to Fe\textsubscript{4} a generalized master equation formalism similar to that used by Leuenberger and Loss\textsuperscript{10} (LLME) to evaluate the relaxation time of Mn\textsubscript{12} at temperature high enough. Good agreement between GME and LLME result is obtained for temperatures $T \gtrsim 2$ K. The scenario we find in Fe\textsubscript{4} is similar to that experimentally observed and theoretically investigated in Mn\textsubscript{12}\textsuperscript{11}. An overall decreasing of the relaxation time at increasing field is modified near to the anticrossing fields by the presence of deep downward spikes.
While the relaxation time at zero external field is heavily affected by both the hyperfine and the dipole fields, this is not the case at finite external field. For this reason we have considered the behaviour of the tetrairon cluster Fe$_4$ in a non zero external magnetic field and we support warmly an experiment to test our theoretical expectation.

**II. TRANSITION PROBABILITY RATE**

The monocrystal made up of tetrairon cluster Fe$_4$ is well simulated by an aggregate of noninteracting spins $S = 5$ with crystal field Hamiltonian

$$\mathcal{H}_s = \mathcal{H}_{\text{cf}} - g\mu_B H_z S_z$$

where $S_z$ is the component of the spin operator along the easy (z) axis; $H_z$ is the magnetic field component along the easy axis, $g = 2$ is the Landé $g$-factor, $\mu_B$ is the Bohr magneton and $\mathcal{H}_{\text{cf}}$ is the “zero field splitting” Hamiltonian

$$\mathcal{H}_{\text{cf}} = B_0^0 O_2^0 + B_4^0 O_4^0 + B_2^2 O_2^2 + B_4^3 O_4^3,$$

where $B_n^m$ are anisotropy parameters and $O_n^m$ are Stevens operator equivalents

$$O_2^0 = 3S_z^2 - S(S + 1),$$

$$O_4^0 = 35S_z^4 - [30S(S + 1) - 25]S_z^2 - 6S(S + 1) + 3[S(S + 1)]^2,$$

$$O_2^2 = \frac{1}{2}(S_+^2 + S_-^2),$$

with $S_\pm = S_x \pm iS_y$ and

$$O_4^3 = \frac{1}{4} [S_z (S_+^3 + S_-^3) + (S_+^3 + S_-^3) S_z].$$

The anisotropy parameters that give the best fit with both the inelastic neutron scattering data and the hysteresis loop of the magnetization were found to be

$B_2^0 = -0.216, B_4^0 = 1.16 \times 10^{-5}, B_2^2 = 0.014$ and $B_4^3 = 7 \times 10^{-4} \text{ K}$. The crystal structure is trigonal with lattice constants $a = 16.1893\text{Å}$ and $c = 52.172\text{Å}$ containing 6 molecules.

From now on we will label $|m^*\rangle$ and $\epsilon_{m^*}$ the eigenstates and the eigenvalues of the crystal field Hamiltonian of Eq. (1) and $|m\rangle$ and $\epsilon_m$ the eigenstates and the eigenvalues of the diagonal part of the crystal field Hamiltonian obtained from Eq. (2) with $B_2^2 = B_4^3 = 0$.  

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Since $B_2^2$ and $B_4^3$ are small with respect to the easy axis anisotropy parameter $B_2^0$ it is expected that $|m^* >$ and $\epsilon_m^*$ do not differ very much from $|m >$ and $\epsilon_m$, respectively. This is true over the whole spectrum of magnetic fields except very close to the anticrossing fields where two unperturbed eigenvalues $\epsilon_m$ and $\epsilon_n$ degenerate. At the anticrossing fields the true states $|m^* >$ and $|n^* >$ are given by $\sim \frac{1}{\sqrt{2}} (|m > \pm |n >)$.

To get the relaxation time of the SMM Fe$_4$, the monocrystal is initially saturated in a large negative magnetic field so that each molecule is in the ground state $|-5^* > \sim | -5 >$. For instance, for $H_z = -2$ T the ground state is $|-5^* > = 0.99998| -5 > - 6.00 \times 10^{-3}| -3 > - 3.72 \times 10^{-3}| -2 > + ...$, where the dots mean the states $|m >$ with $m \neq -5, -3, -2$ the weight of which is between $4 \times 10^{-5}$ and $10^{-9}$.

When the magnetic field is suddenly reversed the initial state is again a state $|-5^* > \sim | -5 >$ (for instance, for $H_z = 0.05$ T one has $|-5^* > = 0.99994| -5 > - 9.23 \times 10^{-3}| -3 > - 6.02 \times 10^{-3}| -2 > + ...$) but it is no longer the ground state which is now the state $|5^* > \sim |5 >$ (for $H_z = 0.05$ T one has $|5^* > = 0.99994|5 > - 8.99 \times 10^{-3}| -3 > - 5.85 \times 10^{-3}|2 > + ...$) so that the initial state relaxes into the ground state in a time $\tau$ owing to the interaction with lattice vibrations. A crucial role is played by the spin-phonon interaction Hamiltonian

$$\mathcal{H}_{sp} = i \sum_{q,\lambda} \sqrt{\frac{\hbar}{2MN\omega_{q\lambda}}} V_{q\lambda}(S)(c_{q\lambda} + c_{q\lambda}^\dagger)$$  \hspace{1cm} (7)$$

where $\hbar$ is the Planck’s constant divided by $2\pi$; the sum is performed over the wavevectors $q$ of the Brillouin zone and over the phonon branches $\lambda$; $N$ is the number of lattice cells; $M$ is the mass of a Fe$_4$ molecule; $\omega_{q\lambda}$ is the phonon dispersion relation of the branch $\lambda$; and $c_{q\lambda}$ and $c_{q\lambda}^\dagger$ are the destruction and creation operators of a phonon of wavevector $q$ belonging to the branch $\lambda$. The spin-phonon potential interaction $V_{q\lambda}(S)$ depends on the phonon variables $(q, \lambda)$ as well as on the spin $S$ of the molecule Fe$_4$. The most general form for a trigonal lattice$^{13}$ is

$$V_{q\lambda}(S) = [A_1(q, \lambda) + iA_2(q, \lambda)]S_x^2 + [A_1(q, \lambda) - iA_2(q, \lambda)]S_y^2$$

$$+ [B_1(q, \lambda) + iB_2(q, \lambda)]\{S_x, S_z\} + [B_1(q, \lambda) - iB_2(q, \lambda)]\{S_x, S_z\}$$ \hspace{1cm} (8)$$

where $\{ , \}$ means anticommutator and

$$A_1(q, \lambda) = \frac{1}{8} g_2(q_x e_q^x - q_y e_q^y)$$ \hspace{1cm} (9)$$

$$A_2(q, \lambda) = \frac{1}{8} g_2(q_x e_q^y + q_y e_q^x)$$ \hspace{1cm} (10)$$
\[ B_1(q, \lambda) = \frac{1}{8} \left[ (g_3 + g_4)q_x e^{z_{q\lambda}} + (g_3 - g_4)q_z e^{x_{q\lambda}} \right], \quad (11) \]
\[ B_2(q, \lambda) = \frac{1}{8} \left[ (g_3 + g_4)q_y e^{z_{q\lambda}} + (g_3 - g_4)q_z e^{y_{q\lambda}} \right]. \quad (12) \]
The magneto-elastic coupling constants \( g_2 \) and \( g_3 \) are connected with the lattice strain while \( g_4 \) is related to the lattice rotation\(^9\); \( e_{q\lambda} \) is the polarization vector associated with the phonon \((q, \lambda)\).

The Fermi’s golden rule for the transition probability rate from a state \( |n^* N \rangle \) to a state \( |m^* N' \rangle \), where \( n^*, m^* \) are the labels characterizing the magnetic wave functions and \( N, N' \) are the labels describing the phonon quantum numbers, reads
\[ W_{m^*, n^*} = \frac{2\pi}{\hbar} \sum_{q, \lambda} \left| < m^* N'|H_{sp}|n^* N > \right|^2 p_N \delta(E_N - E_{N'} + \epsilon_{n^*} - \epsilon_{m^*}) \quad (13) \]
where \( E_N \) and \( E_{N'} \) are the eigenvalues of the phonon Hamiltonian; \( p_N \) is the thermal weight of the initial phonon state \( |N \rangle \). Using the spin-phonon Hamiltonian (7) one obtains
\[ W_{m^*, n^*} = \frac{2\pi}{\hbar} \sum_{q, \lambda} \left( \frac{\hbar}{2M N \omega_{q\lambda}} \right) | < m^* | V_{q\lambda}(S) | n^* > |^2 \]
\[ \left[ (1 + n_{q\lambda}) \delta(\hbar \omega_{q\lambda} + \epsilon_{m^*} - \epsilon_{n^*}) + n_{q\lambda} \delta(\hbar \omega_{q\lambda} - \epsilon_{m^*} + \epsilon_{n^*}) \right] \quad (14) \]
where \( n_{q\lambda} = [e^{\beta \hbar \omega_{q\lambda}} - 1]^{-1} \) is the thermal average of the phonon occupation number with \( \beta = (k_B T)^{-1} \), where \( k_B \) is the Boltzmann constant and \( T \) the absolute temperature. To perform the sum over \( \lambda \) and \( q \) in Eq. (14) we restrict ourselves to the three acoustic branches and to the long wavelength region of the spectrum. Both restrictions are justified by the very low temperature at which the experiment on Fe\(_4\) is performed \((T \lesssim 4K)\). Supposing that the dispersion relation is \( \hbar \omega_{q\lambda} = \sqrt{c_+^2 (q_x^2 + q_y^2) + c_\parallel^2 q_z^2} \), where \( c_+ \) and \( c_\parallel \) are the sound velocities of phonons propagating in the \( xy \)-plane and parallel to the \( z \)-axis, respectively, Eq.(14) gives
\[ W_{m^*, n^*} = \frac{1}{96\pi \rho \hbar^4} \left\{ \frac{g_3^2}{c_\perp^2 c_\parallel^2} [(< m^* | S_+^2 | n^* >)^2 + (< m^* | S_-^2 | n^* >)^2] + \right. \]
\[ \left. + \frac{1}{2} \left[ \frac{(g_3 - g_4)^2}{c_\perp^2 c_\parallel^2} + \frac{(g_3 + g_4)^2}{c_\perp^2 c_\parallel^2} \right] [(< m^* | \{S_-, S_z\} | n^* >)^2 \right. \]
\[ + (< m^* | \{S_+, S_z\} | n^* >)^2] \right\} (\epsilon_{m^*} - \epsilon_{n^*})^3 n \left( \frac{\epsilon_{m^*} - \epsilon_{n^*}}{k_B T} \right) \quad (15) \]
where \( \rho = M/V_c \) is the density; \( n(x) = (e^x - 1)^{-1} \). Note that for \( \epsilon_{m^*} < \epsilon_{n^*} \) it is convenient to make use of the following identity
\[ (\epsilon_{m^*} - \epsilon_{n^*})^3 n \left( \frac{\epsilon_{m^*} - \epsilon_{n^*}}{k_B T} \right) = (\epsilon_{n^*} - \epsilon_{m^*})^3 \left[ 1 + n \left( \frac{\epsilon_{m^*} - \epsilon_{n^*}}{k_B T} \right) \right] . \quad (16) \]
Since there are no experimental data about the magneto-elastic constants $g_n$ appearing in Eq.(15) we assume $g_2 \simeq g_3 \simeq g_4 = g$ so that the transition probability rate reads

$$ W_{m^*,n^*} = A \, p(m^*,n^*) \, n \left( \frac{\epsilon_{m^*} - \epsilon_{n^*}}{k_B T} \right) $$

(17)

where

$$ A = \frac{g^2}{96 \pi \hbar^2 c_\perp^4 c_\parallel} $$

(18)

and

$$ p(m^*,n^*) = \left[ (\langle m^*|S^2|n^* \rangle)^2 + (\langle n^*|S^2|m^* \rangle)^2 \right] \frac{1}{k_B T} \left( \epsilon_{m^*} - \epsilon_{n^*} \right)^3 $$

(19)

The coupling constant $A = 1529 \text{ K}^{-3} \text{s}^{-1}$ is chosen to fit the relaxation time $\tau = 1.7 \times 10^{-6} \text{ s}$ at $T = 4 \text{ K}$ and $H_z = 0 \text{ T}$.

### III. RELAXATION TIME AT T=0

From Eqs. (15) and (16) one sees that at $T = 0$ the only nonvanishing transition probability rates are $W_{m^*,-5^*}$ for which $\epsilon_{m^*} < \epsilon_{-5^*}$. The relaxation time is the inverse of the sum of all the transition probability rates from the initial state $|-5^*\rangle$ to the states $|m^*\rangle$ that is

$$ \tau = \frac{1}{\sum_{m^*} W_{m^*,-5^*}} $$

(20)

Even for magnetic fields far from the anticrossing fields where $|m^*\rangle \simeq |m\rangle$ the replacement of the eigenstates $|m^*\rangle$ with the eigenstates $|m\rangle$ leads to transition probability rates equal to zero and to an infinite relaxation time because of the nature of the spin-phonon interaction.

For $0 < H_z < H_1$, where $H_1 = 0.477 \text{ T}$ is the anticrossing field between the states $|4^*\rangle$ and $|-5^*\rangle$ corresponding to the minimum splitting $\Delta_{-5,4} = \epsilon_{-5^*}(H_1) - \epsilon_{4^*}(H_1)$. The state $|-5^*\rangle$ is the first excited state so that the only non zero transition probability rate is $W_{5^*,-5^*}$ that is

$$ W_{5^*,-5^*} = A \, p(-5^*,5^*) $$

(21)

Note the crucial role played by the non diagonal terms of the crystal field Hamiltonian proportional to $B_2^4$ and $B_4^2$ that cause a mixing between the states $|m\rangle$. Indeed neglecting these terms, the eigenstates of the crystal field Hamiltonian reduce to the states $|m\rangle$ and because
of the nature of the spin-phonon coupling (8) the only non vanishing transition probability rates are those between nearest levels \( W_{m\pm 1,m} \) and next-nearest levels \( W_{m\pm 2,m} \). This implies that the system starting from the state \(|-5>\) must overcome the energy barrier between the states \(|-5>\) and \(|5>\) to relax into the final state \(|5>\). This could happen only if the magnetic system *receives* energy from the phonon bath, an event impossible at \( T = 0 \) K, so that the relaxation time goes to infinity for \( T \rightarrow 0 \). On the contrary the weak mixing entered by \( B_2^2 \) and \( B_4^3 \) is sufficient to give a non zero transition probability rate \( W_{5^*,-5^*} \) corresponding to a direct quantum tunneling between states \(|-5^*>\) and \(|5^*>\) during which the magnetic system *gives* energy to the phonon bath so that relaxation occurs even for \( T \rightarrow 0 \). For weak magnetic fields \( \epsilon_{-5^*} - \epsilon_{5^*} \approx 10 g \mu_B H_z \) so that \( p(-5^*,5^*) \propto H_z^2 \) in agreement with the behaviour expected\(^9\) for the nanomagnet \( \text{Mn}_{12} \).

In Table I we give the \( p(-5^*,m^*) \) for several magnetic fields. To get the relaxation time one has to sum the elements of each row, multiply the sum by \( A = 1529 \) K\(^{-3}\) s\(^{-1}\) and take the inverse. As one can see from Table I the first column corresponding to \( p(-5^*,5^*) \) is complete since the ground state energy \( \epsilon_{5^*} \) is always below the initial state energy \( \epsilon_{-5^*} \). The second column corresponding to \( p(-5^*,4^*) \) appears at \( H_1 = 0.477 \) T, where also the energy \( \epsilon_{4^*} \) becomes lower than \( \epsilon_{-5^*} \). At \( H_2 = 0.959 \) T, the second anticrossing field, also the energy \( \epsilon_{3^*} \) becomes lower than \( \epsilon_{-5^*} \) so that the transition \( p(-5^*,3^*) \) appears (third column of Table I). At each anticrossing field a new transition occurs. The columns corresponding to \( p(-5^*,2^*), p(-5^*,1^*) \) and \( p(-5^*,0^*) \) appear at \( H_3 = 1.44, H_4 = 1.93 \) and \( H_5 = 2.41 \) T, respectively. Note that \( p(-5^*,5^*) \) is the main contribution for \( 0 < H_z \lesssim 1 \) T; \( p(-5^*,4^*) \) dominates for \( 1.1 \lesssim H_z \lesssim 1.5 \) T, \( p(-5^*,2^*) \) for \( 2 \lesssim H_z \lesssim 2.7 \) T.

The relaxation time vs field is shown in the semi-log plot of Fig. 1. Two main features have to be pointed out: the large increasing of the relaxation time for \( H_z \rightarrow 0 \) and the deep downward spikes at the anticrossing fields \( H_z = H_n \) with \( n = 5 - m \) and \( m = 4,3,\ldots,0,-1 \).

The growth of the relaxation time for \( H_z \rightarrow 0 \) is a consequence of the fact that \( p(-5^*,5^*) \) is proportional to \( (\epsilon_{-5^*} - \epsilon_{5^*})^3 \) where \( \epsilon_{-5^*} - \epsilon_{5^*} \approx \sqrt{(\Delta_{-5,5})^2 + (10g \mu_B H_z)^2} \) with \( \Delta_{-5,5}/k_B = 5.03 \times 10^{-7} \) K. For magnetic fields \( H_z \gtrsim 10^{-7} \) T \( (g \mu_B H_z \approx \Delta_{-5,5}) \) one has \( \epsilon_{-5^*} - \epsilon_{5^*} \approx 10g \mu_B H_z \) and \( \tau \approx (H_z)^{-3} \). For \( H_z \lesssim 10^{-7} \) T, however, \( \epsilon_{-5^*} - \epsilon_{5^*} \approx \Delta_{-5,5} \) and \( \tau \approx (\Delta_{-5,5})^{-3} \). In particular \( \tau(0 \text{K},0 \text{T}) = 9.02 \times 10^{19} \) s. Any attempt to check this pseudo-divergence at \( H_z = 0 \) in the actual compound is prevented by the existence of local magnetic fields due to hyperfine and dipole interaction as discussed\(^9\) for \( \text{Mn}_{12} \). In the tetrairon cluster \( \text{Fe}_4 \) the
\begin{table}[h]
\centering
\caption{Transitions $p(-5^*, m^*)(K^3)$.} \\
\begin{tabular}{cccccccc}
\hline
$H_z$(T) & $p(-5^*, 5^*)$ & $p(-5^*, 4^*)$ & $p(-5^*, 3^*)$ & $p(-5^*, 2^*)$ & $p(-5^*, 1^*)$ & $p(-5^*, 0^*)$ \\
\hline
0.1 & 1.24&$\times$10$^{-8}$ & & & & & \\
0.2 & 1.06&$\times$10$^{-7}$ & & & & & \\
0.3 & 4.05&$\times$10$^{-7}$ & & & & & \\
0.4 & 1.24&$\times$10$^{-6}$ & & & & & \\
0.5 & 6.37&$\times$10$^{-6}$ & 2.80&$\times$10$^{-9}$ & & & \\
0.6 & 6.85&$\times$10$^{-6}$ & 4.85&$\times$10$^{-7}$ & & & \\
0.7 & 1.74&$\times$10$^{-5}$ & 3.82&$\times$10$^{-6}$ & & & \\
0.8 & 5.83&$\times$10$^{-5}$ & 2.21&$\times$10$^{-5}$ & & & \\
0.9 & 5.09&$\times$10$^{-4}$ & 3.07&$\times$10$^{-4}$ & & & \\
1 & 1.22&$\times$10$^{-3}$ & 1.61&$\times$10$^{-3}$ & 7.60&$\times$10$^{-7}$ & & \\
1.1 & 1.13&$\times$10$^{-4}$ & 5.16&$\times$10$^{-4}$ & 3.14&$\times$10$^{-5}$ & & \\
1.2 & 4.01&$\times$10$^{-5}$ & 8.72&$\times$10$^{-4}$ & 1.72&$\times$10$^{-4}$ & & \\
1.3 & 2.01&$\times$10$^{-5}$ & 2.97&$\times$10$^{-3}$ & 6.75&$\times$10$^{-4}$ & & \\
1.4 & 3.43&$\times$10$^{-5}$ & 4.30&$\times$10$^{-2}$ & 8.69&$\times$10$^{-3}$ & & \\
1.5 & 4.60&$\times$10$^{-5}$ & 3.48&$\times$10$^{-2}$ & 1.53&$\times$10$^{-2}$ & 1.55&$\times$10$^{-4}$ & \\
1.6 & 1.68&$\times$10$^{-5}$ & 6.68&$\times$10$^{-3}$ & 1.01&$\times$10$^{-2}$ & 3.76&$\times$10$^{-3}$ & \\
1.7 & 1.62&$\times$10$^{-5}$ & 3.84&$\times$10$^{-3}$ & 1.81&$\times$10$^{-2}$ & 1.99&$\times$10$^{-2}$ & \\
1.8 & 3.22&$\times$10$^{-5}$ & 3.39&$\times$10$^{-3}$ & 5.33&$\times$10$^{-2}$ & 6.87&$\times$10$^{-2}$ & \\
1.9 & 5.13&$\times$10$^{-4}$ & 6.47&$\times$10$^{-3}$ & 0.993 & 0.240 & & \\
2 & 1.56&$\times$10$^{-4}$ & 2.89&$\times$10$^{-3}$ & 0.130 & 0.555 & 1.19&$\times$10$^{-3}$ & \\
2.1 & 1.58&$\times$10$^{-4}$ & 5.05&$\times$10$^{-3}$ & 2.68&$\times$10$^{-2}$ & 1.53 & 1.34&$\times$10$^{-2}$ & \\
2.2 & 4.19&$\times$10$^{-4}$ & 1.08&$\times$10$^{-2}$ & 3.03&$\times$10$^{-2}$ & 5.11 & 4.76&$\times$10$^{-2}$ & \\
2.3 & 2.04&$\times$10$^{-3}$ & 4.06&$\times$10$^{-2}$ & 0.104 & 27.4 & 0.138 & \\
2.4 & 0.267 & 4.29 & 10.1 & 3.80&$\times$10$^3$ & 17.9 & & \\
2.5 & 6.13&$\times$10$^{-3}$ & 8.61&$\times$10$^{-2}$ & 0.172 & 90.5 & 2.43 & 0.175 & \\
2.6 & 1.90&$\times$10$^{-3}$ & 2.67&$\times$10$^{-2}$ & 5.17&$\times$10$^{-2}$ & 28.7 & 3.59 & 1.94 & \\
2.7 & 1.16&$\times$10$^{-3}$ & 2.15&$\times$10$^{-2}$ & 5.89&$\times$10$^{-2}$ & 18.8 & 9.66 & 8.34 & \\
2.8 & 9.82&$\times$10$^{-4}$ & 4.78&$\times$10$^{-2}$ & 0.193 & 14.6 & 54.1 & 26.1 & \\
\hline
\end{tabular}
\end{table}
FIG. 1: Semi-log plot of the relaxation time $\tau$ at $T = 0$K vs magnetic field for crystal field parameters $B_2^0 = -0.216$K, $B_4^0 = 1.16 \times 10^{-5}$K, $B_2^2 = 0.014$K and $B_4^3 = 7 \times 10^{-4}$K.

The hyperfine field should be $H_{\text{hyp}} \lesssim 4 \times 10^{-5}$ T since only 2% of the natural iron has a nuclear spin $I = 1/2$. From the crystal data we estimate that the dipolar field between two Fe$_4$ molecules is $H_{\text{dip}} \sim 4 \times 10^{-3}$ T that is two orders of magnitude greater than the hyperfine field. If we suppose that all 6 nearest neighbour molecules Fe$_4$ have the magnetic moment directed along the positive z-axis, a dipolar field of order $H_{\text{dip}} \sim 0.025$ T is obtained. This should imply that at zero external field a transition to an ordered phase is expected at $T_{\text{dip}} \sim 0.16$ K not observed experimentally. So we think that the dipole-dipole interaction between Fe$_4$ molecules, neglected in our approach, may become dominant for $H_z \lesssim 0.01$ T for which we find $\tau(0$K, $0.01$T) = $5.37 \times 10^7$ s. The relaxation time in zero magnetic field shows a saturation to a value of about 1500 s for $T \lesssim 0.2$ K. We obtain such a value for $H_z \approx 0.3$ T more than an order of magnitude greater than the expected dipolar field.

The deep downward spikes shown in Fig. 1 at the anticrossing fields are originated by the strong mixing of the states $| - 5 >$ and $| m >$ at $H_n = H_{5-m}$ appearing in the eigenstate $| - 5^* >$. In particular, the mixing concerns the states $| - 5 >$ and $| 4 >$ at $H_1$, $| - 5 >$ and $| 3 >$ at $H_2$, and so on. The strong mixing of the wave functions leads to a large increase of
$p(-5^*, 5^*)$ for $H_z \rightarrow H_1$ owing to the term $< 4|\{S_-, S_z\}|5>$ in Eq. (19) and for $H_z \rightarrow H_2$ owing to the term $< 3|S_z^2|5>$ in Eq. (19). Similarly the strong increase of $p(-5^*, 4^*)$ for $H_z \rightarrow H_2$ and $H_z \rightarrow H_3$ is due to the terms $< 3|\{S_-, S_z\}|4>$ and $< 2|S_z^2|4>$, respectively. Similar considerations can be done for any $p(-5^*, m^*)$ so that a sudden decrease of the relaxation time is expected around any anticrossing magnetic fields. In the actual compound we think that the presence of hyperfine and dipolar field only spread the resonance about the anticrossing field but the spikes, possibly reduced, cannot disappear. We hope that a measure of the relaxation time of Fe$_4$ vs field at low temperature ($T \lesssim 0.2$ K) may be done to check our expectation. Indeed such an experiment was done in Mn$_{12}$ for $T \sim 2$ K where resonance dips were recorded$^{11}$.

IV. MASTER EQUATION

In this Section we propose a generalized master equation (GME) that accounts for quantum tunneling at finite temperature taking advantage from the zero temperature rigorous results of the previous Section. To get the GME we use the master equation formalism$^6$ according to which the time evolution of the probability $\rho_{m^*}(t)$ of finding the molecule Fe$_4$ in the level $|m^*>$ with energy $\epsilon_{m^*}$ at the time $t$ is given by

$$\dot{\rho}_{m^*} = \sum_{n^*} W_{m^*,n^*}\rho_{n^*} - \rho_{m^*} \sum_{n^*} W_{n^*,m^*}.$$  \hspace{1cm} (22)

As one can see from Eq. (22) the probability $\rho_{m^*}$ increases in time owing to transitions from all other states $|n^*>$ to $|m^*>$ and decreases owing to transition from the state $|m^*>$ to all other states $|n^*>$. All transitions are ruled by the transition probability rates $W_{n^*,m^*}$ given by Eq. (17). The standard master equation (SME)$^7$ replaces $|m^*>$ by $|m>$ and $\epsilon_{m^*}$ by $\epsilon_m$; the replacement of the eigenvalues and the eigenstates of the crystal field Hamiltonian with the eigenvalues and the eigenstates of its diagonal part is justified by the fact that the non-diagonal terms are generally much smaller than the diagonal ones. Neglecting terms proportional to $B_2^2$, $B_4^2$ in Eq. (2) the master equation (22) becomes

$$\dot{\rho}_m = \sum_n' W_{m,n}\rho_n - \rho_m \sum_n' W_{n,m},$$  \hspace{1cm} (23)

where $m = -5, ..., 5$. The initial conditions are $\rho_m(0) = 0$ for each $m \neq -5$ and $\rho_{-5}(0) = 1$. The prime on the sum means that $n$ is restricted to $n = m \pm 1, m \pm 2$. Indeed the nature of
the spin-phonon interaction (8) makes all transition probability rates zero except

\[ W_{m\pm 1,m} = 2A(2m \pm 1)^2(5 \mp m)(5 \pm m + 1)(\epsilon_{m\pm 1} - \epsilon_m)^3 n \left( \frac{\epsilon_{m\pm 1} - \epsilon_m}{k_BT} \right) \]  

(24)

and

\[ W_{m\pm 2,m} = A(5 \mp m)(5 \mp m - 1)(5 \pm m + 1)(5 \pm m + 2)(\epsilon_{m\pm 2} - \epsilon_m)^3 n \left( \frac{\epsilon_{m\pm 2} - \epsilon_m}{k_BT} \right) \]  

(25)

The detailed set of \( 2S + 1 = 11 \) equations is given in the Appendix A. The ansatz

\[ \rho_m(t) = \sum_{l=1}^{2S+1} r_m^{(l)} e^{\lambda_l t} \]  

(26)

reduces the solution of the system of differential equations (23) to finding the \( 2S + 1 = 11 \) eigenvalues of the matrix \( W(0) \) given by Eq. (A23). All the eigenvalues of the matrix \( W(0) \) are real and negative except one, say \( \lambda_{11} \), which is zero. This is consistent with the fact that for \( t \to \infty \) all probabilities \( \rho_m(t) \) must converge to their statistical equilibrium values

\[ \rho_m(t \to \infty) = r_m^{(11)} = \frac{e^{-\beta \epsilon_m}}{\sum_n e^{-\beta \epsilon_n}}. \]  

(27)

The overall relaxation time is given by the reciprocal of the smallest (in magnitude) non zero eigenvalue, say \( \lambda_{10} \), that is

\[ \tau = \frac{1}{|\lambda_{10}|}. \]  

(28)

At fixed magnetic field we see that the relaxation time vs temperature satisfies an Arrhenius law of the type

\[ \tau(T, H_z) = \tau_0(H_z)e^{\frac{U(H_z)}{T}} \]  

(29)

where \( U(H_z) \) is of the order of the energy barrier between the states \(|\pm 5>\). From now on the energies are measured in Kelvin degrees. We find \( \tau_0(H_z) = (3.1 \pm 0.1) \times 10^{-8}, (4.3 \pm 0.2) \times 10^{-8}, (6.0 \pm 0.3) \times 10^{-8} \) s, and \( U(H_z) = 16.32 \pm 0.03, 15.41 \pm 0.05, 14.06 \pm 0.05 \) K, for \( H_z = 0.05, 0.2, 0.4 \) T, respectively. Note that a fit of the data\(^2\) with the Arrhenius law for \( T \gtrsim 1.9 \) K and \( H_z = 0 \) gives \( \tau_0 = (3.4 \pm 0.2) \times 10^{-8} \) s and \( U = 15.6 \pm 0.2 \) K. The Arrhenius law does not fit the experimental data for \( T \lesssim 1 \) K and the relaxation time is found to saturate for \( T \lesssim 0.2 \) K owing to quantum tunneling\(^2\) in presence of spin-phonon interaction.

To account for quantum corrections at very low temperature we start with the master equation (22) keeping the most important quantum contribution deduced by Table I and
Eq. (17). Since the transition probability rates \(W_{m^*\pm 1,m^*}\) and \(W_{m^*\pm 2,m^*}\) are the most important ones at finite temperature and they do not differ very much from the corresponding \(W_{m\pm 1,m}\) and \(W_{m\pm 2,m}\) we simply add the appropriate quantum transition probability rates \(W_{m^*,-5^*}\) and \(W_{-5^*,m^*}\) to the SME of Eq. (23) leading to a new generalized master equation (GME). The selection of the transition probability rates is a consequence of the initial conditions of the experiment where each molecule is prepared in the state \(\ket{-5^*}\) because of the application of a large negative magnetic field. Details of calculations are given in the Appendix B.

![Graph](image)

**FIG. 2:** Semi-log plot of the relaxation time \(\tau\) (s) and \(\tau_u = 1\) s for \(H_z = 0.05\) T vs the reciprocal of the temperature \(1/T\) (K\(^{-1}\)) for \(A = 1529\) K\(^{-3}\) s\(^{-1}\).

The relaxation time is the reciprocal of the smallest (in magnitude) non zero eigenvalue \(\lambda_{10}\) of the matrix \(W^{(n)}\) with \(n = 1, 2, ..., 6\) given in the Appendix B. Fig. 2 shows the relaxation time vs temperature for \(H_z = 0.05\) T obtained from \(W^{(1)}\). As one can see the relaxation time follows an Arrhenius law for \(T \gtrsim 0.6\) K \((\tau = 3.1 \times 10^{-8} e^{15/4} \text{ s})\) and saturates to the value \(\tau = 4.272 \times 10^5\) s for \(T \to 0\).

In Figs. 3, 4 and 5 the relaxation time vs field is shown for \(T = 0.6, 1\) and \(2\) K, respectively. Full circles are obtained from the standard master equation corresponding to \(W^{(0)}\) (Appendix A); (red) squares are obtained from \(W^{(1)}\) \((0 < H_z < 1\) T\) where the quantum effect \(p(-5^*,5^*)\) is taken into account (see Appendix B). For \(1 < H_z < 1.6\) T we see from
FIG. 3: (Color on line) Semi-log plot of the relaxation time $\tau$ at $T = 0.6\text{K}$ vs magnetic field. Full (black) circles: standard master equation (SME); (red) squares: generalized master equation (GME) with $p(-5^*, 5^*)$; (blue) diamonds: GME with $p(-5^*, 4^*)$; (green) up-triangles: GME with $p(-5^*, 3^*)$; (cyan) down-triangles: GME with $p(-5^*, 2^*)$; (magenta) stars: GME with $p(-5^*, 1^*)$.

Table I that the dominant quantum contribution comes from $p(-5^*, 4^*)$ and the matrix $W^{(2)}$ is used to draw the (blue) diamonds. In the same way (green) up-triangles ($1.6 < H_z < 2\text{ T}$), (cyan) down-triangle ($2 < H_z < 2.7\text{ T}$) and (magenta) stars ($H_z > 2.7\text{ T}$) are obtained accounting for $p(-5^*, 3^*)$, $p(-5^*, 2^*)$ and $p(-5^*, 1^*)$, making use of matrices $W^{(3)}$, $W^{(4)}$ and $W^{(5)}$, respectively. The main discrepancies between the standard and quantum result are confined close to the anticrossing fields where the deep spikes found at $T = 0\text{ K}$ (see Fig. 1) are only slightly reduced. No trace of the pseudo-divergence for $H_z \to 0$ is obtained at variance with the zero temperature result.

As one can see at increasing temperature the relaxation time decreases and the width of the downward spikes shrinks so that for temperature $T \simeq 2\text{ K}$ only the spikes corresponding to the anticrossing fields $H_5$ and $H_6$ could be observed experimentally. For higher temperatures the thermal activated relaxation dominates the quantum tunneling effects.

For weak magnetic field and very low temperature, we are able to give an analytic expres-
FIG. 4: (Color on line) Semi-log plot of the relaxation time \( \tau \) at \( T = 1 \) K vs magnetic field. Full (black) circles: SME; (red) squares: GME with \( p(-5^*, 5^*) \); (blue) diamonds: GME with \( p(-5^*, 4^*) \); (green) up-triangles: GME master with \( p(-5^*, 3^*) \); (cyan) down-triangles: GME with \( p(-5^*, 2^*) \); (magenta) stars: GME with \( p(-5^*, 1^*) \).

Expression for the total transition probability rate \( W_{\text{tot}} \). Indeed the leading terms that contribute to the depletion of the eigenstate \( | -5^* \rangle \) come from the transitions to the states \( |5^* \rangle \) and \( | -4^* \rangle \) that is

\[
W_{\text{tot}} \simeq W_{5^*, -5^*} + W_{-4^*, -5^*} \tag{30}
\]

where \( W_{5^*, -5^*} \simeq A p(-5^*, 5^*) \) is small (see Table I) but finite while

\[
W_{-4^*, -5^*} \simeq W_{-4, -5} = 1.62 \times 10^3 A (5.77 - 1.34H_z)^3 n \left( \frac{5.77 - 1.34H_z}{T} \right) \tag{31}
\]

goes to zero for \( T \to 0 \) owing to the occupation number. In Eq. (31) the energy is measured in K and \( g\mu_B/k_B \) is replaced by its value 1.34 K/T so that the magnetic field \( H_z \) is measured in Tesla. Note that the pre-factor \( p(-5, -4) \) is several orders of magnitude greater than \( p(-5^*, 5^*) \). For instance, for \( H_z = 0.05 \) T we have

\[
W_{\text{tot}} \simeq A \left[ 1.53 \times 10^{-9} + 3.01 \times 10^5 n \left( \frac{5.71}{T} \right) \right]. \tag{32}
\]
FIG. 5: (Color on line) Semi-log plot of the relaxation time \( \tau \) at \( T = 2 \) K vs magnetic field. Full (black) circles: SME; (red) squares: GME with \( p(-5^*, 5^*) \); (blue) diamonds: GME with \( p(-5^*, 4^*) \); (green) up-triangles: GME with \( p(-5^*, 3^*) \); (cyan) down-triangles: GME with \( p(-5^*, 2^*) \); (magenta) stars: GME with \( p(-5^*, 1^*) \).

Defining a crossover temperature \( T_0 \) between the quantum regime and the thermal activated one (where the relaxation time follows an Arrhenius law) as the temperature at which the two contributions are comparable, Eq. (32) gives \( T_0 \simeq 0.17 \) K in good agreement with the crossover temperature of the experiment\(^2\).

To get the relaxation time of Mn\(_{12}\) for \( T \gtrsim 1 \) K Leuenberger and Loss\(^{10}\) proposed a different generalized master equation (LLME) in which phonon induced spin transitions between levels \( \epsilon_m \) and \( \epsilon_{m\pm 1} \) and between \( \epsilon_m \) and \( \epsilon_{m\pm 2} \) as well as resonant tunneling caused by the non diagonal part of the crystal field Hamiltonian are taken into account. The LLME reads

\[
\dot{\rho}_m = \frac{i}{\hbar} < m | [\rho, \mathcal{H}_{cf}]| m > + \sum_n W_{m,n} \rho_n - \rho_m \sum_n W_{n,m}. \tag{33}
\]

where \([ , ]\) is the commutator that accounts for quantum effects. A degenerate level perturbation theory is applied to a suitable order to give a non zero splitting between the two unperturbed levels with the same energy at the anticrossing field. A projection of the crystal
field Hamiltonian into the subspace of these two levels is then performed so that the number of the off-diagonal elements generated by the commutation rules is drastically reduced. We apply the LLME to the tetrairon cluster Fe\textsubscript{4} restricting to $\rho_{-5,m}$ and $\rho_{m,-5}$ where $|-5>$ and $|m>$ are the crossing states at the field $H_n \equiv H_{5-m}$ and using an effective Hamiltonian as illustrated in the Appendix B. Taking advantage from the very short time decaying of the off-diagonal elements of the density matrix the LLME is obtained from the GME by replacing both $W_{-5*,m*}$ and $W_{m*,-5*}$ appearing in GME with $\Gamma_{-5}^m$ where

$$\Gamma_{-5}^m = \left( \frac{\Delta_{-5,m}}{\hbar} \right)^2 \frac{\sum_{n'}' (W_{n,m} + W_{n,-5})}{\left[ \sum_{n'}' (W_{n,m} + W_{n,-5}) \right]^2 + \left[ \frac{2g\mu_B H_z}{\hbar} (5 + m) \right]^2}$$

(34)

Note that $g\mu_B / \hbar = 1.76 \times 10^{11} (\text{Ts})^{-1}$.

In Figs. 6, 7 and 8 we show the relaxation time obtained from the LLME of the Appendix B for $T = 0.6$, 1 and 2 K, respectively. The SME result is shown for comparison using (black) full circles. The (red) squares, (blue) diamonds, (green) up-triangles, (cyan) down-triangles, (magenta) stars: LLME with $\Gamma_{-5}^1$; open circles: LLME with $\Gamma_{-5}^0$. 

FIG. 6: (Color on line) Semi-log plot of the relaxation time $\tau$ at $T = 0.6$K vs magnetic field. Full (black) circles: SME; (red) squares: LLME with $\Gamma_{-5}^5$; (blue) diamonds: LLME with $\Gamma_{-5}^4$; (green) up-triangles: LLME with $\Gamma_{-5}^3$; (cyan) down-triangles: LLME with $\Gamma_{-5}^2$; (magenta) stars: LLME with $\Gamma_{-5}^1$; open circles: LLME with $\Gamma_{-5}^0$. 

In Figs. 6, 7 and 8 we show the relaxation time obtained from the LLME of the Appendix B for $T = 0.6$, 1 and 2 K, respectively. The SME result is shown for comparison using (black) full circles. The (red) squares, (blue) diamonds, (green) up-triangles, (cyan) down-triangles,
FIG. 7: (Color on line) Semi-log plot of the relaxation time $\tau$ at $T = 1$ K vs magnetic field. Full (black) circles: SME; (red) squares: LLME with $\Gamma_{5,5}^5$; (blue) diamonds: LLME with $\Gamma_{4,5}^4$; (green) up-triangles: LLME with $\Gamma_{3,5}^3$; (cyan) down-triangles: LLME with $\Gamma_{2,5}^2$; (magenta) stars: LLME with $\Gamma_{1,5}^1$; open circles: LLME with $\Gamma_{0,5}^0$. 

(magenta) stars and open circles are obtained from the LLME with $\Gamma_{5,5}^5$, $\Gamma_{4,5}^4$, $\Gamma_{3,5}^3$, $\Gamma_{2,5}^2$, $\Gamma_{1,5}^1$ and $\Gamma_{0,5}^0$, respectively.

Comparing Figs. 3 and 6, 4 and 7, 5 and 8 an overall good agreement between the results obtained from the GME and LLME is seen. Spikes in correspondence of the anticrossing fields are found in both the GME and LLME. Quantitatively the spikes obtained from the GME are deeper than those obtained from the LLME. The main discrepancy is found at $H_z = 0$ where the LLME leads to a downward spike for $T = 0.6$ and 1 K whereas in the GME no spike at all is found at $H_z = 0$. This can be explained noticing that $\Gamma_{5,5}^5$ at low temperature and zero field is given by

$$\Gamma_{5,5}^5 \simeq \left(\frac{\Delta_{-5,5}}{\hbar}\right)^2 \frac{1}{2W_{4,5}} \simeq 5.31 \, e^{5.77} \, s^{-1}$$

(35)

so that $\Gamma_{5,5}^5 \to \infty$ for $T \to 0$ and the relaxation time goes to zero. This seems to be an
FIG. 8: (Color on line) Semi-log plot of the relaxation time \( \tau \) at \( T = 2 \) K vs magnetic field. Full (black) circles: SME; (red) squares: LLME with \( \Gamma_{5-5} \); (blue) diamonds: LLME with \( \Gamma_{4-5} \); (green) up-triangles: LLME with \( \Gamma_{3-5} \); (cyan) down-triangles: LLME with \( \Gamma_{2-5} \); (magenta) stars: LLME with \( \Gamma_{1-5} \); open circles (◦): LLME with \( \Gamma_{0-5} \).

artefact of the approximation. Indeed for \( T \to 0 \) but \( H_z \neq 0 \) one has

\[
\Gamma_{5-5} \simeq \left( \frac{\Delta_{-5,5}}{\hbar} \right)^2 \frac{W_{4,5}}{2 \left( \log \mu B H_z \right)^2} \simeq 3.34 \times 10^{-7} \frac{e^{-\frac{\Delta_{-5,5}}{\hbar}}}{H_z^2} \text{s}^{-1}
\]

(36)

so that \( \Gamma_{5-5} \to 0 \) for \( T \to 0 \) leading to a divergent relaxation time. Such a result does not recover the quantum result according to which the relaxation time is finite at \( T = 0 \) K. This inconvenience is not found for the other anticrossing fields. For instance at \( H_z = H_1 \) and low temperature \( \Gamma_{4-5} \) saturates to the value

\[
\Gamma_{4-5} \simeq \left( \frac{\Delta_{-5,4}}{\hbar} \right)^2 \frac{1}{W_{5,4}} \simeq 10^2 \text{s}^{-1}
\]

(37)

so that \( \tau \simeq 10^{-2} \) s. This saturation value seems to have been reached at \( T = 0.6 \) K as shown in Fig. 6. For comparison the transition probability rate obtained directly from Eq. (21) is \( W_{5,-5} = 3.8 \times 10^8 \) s\(^{-1} \) so that \( \tau \simeq 2.7 \times 10^{-9} \) s while at \( T = 0.6, 1, 2 \) K the relaxation time is \( \tau \simeq 1.2 - 1.5 \times 10^{-8} \) s.
V. SUMMARY AND CONCLUSIONS

A theory that gives both the saturation of the relaxation time of the magnetization at very low temperature and the Arrhenius law at higher temperature has been formulated. A crucial role is played by the use of the eigenstates $|m^*\rangle$ of the crystal field Hamiltonian instead of the eigenstates $|m\rangle$ of its diagonal part in the evaluation of the transition probability rates induced by the spin-phonon interaction. The use of the exact eigenstates allows to obtain finite transition probability rates for $T \to 0$ owing to quantum tunneling. Moreover the master equation written in term of density matrix elements on the basis $|m^*\rangle$ seems to be a very good starting point to obtain the relaxation time at finite temperature. An investigation of the transition probability rate at $T = 0$ K allows us to simplify considerably the problem keeping only the dominant transition probability rate related to $p(-5^*, m^*)$, the choice of $m^*$ being suggested by Table I. The choice of the main transition probability rate leads to a generalized master equation (GME) that recovers both the saturation of the relaxation time at low temperature and the Arrhenius law at higher temperature in agreement with the experiment on Fe$_4$. Also the crossover temperature between the two regimes is found to be in very good agreement with the experiment. The relaxation time versus field at $T = 0$ shows deep downward spikes close to the anticrossing fields (see Fig. 1), a sign of the quantum tunneling at zero temperature. These spikes are present also at finite temperature as shown in Figs. 3-6. A problem arises around $H_z = 0$ since the existence of hyperfine (weak in Fe$_4$) and dipolar fields prevents any check of the present theory for $H_z \lesssim 0.01$ T where the saturation value of the relaxation time, however, is orders of magnitude greater than that measured at $H_z = 0$. Comparison between the GME and the generalized master equation proposed by Leuenberger and Loss$^{10}$ (LLME) to explain the field dependent relaxation time of the magnetization in Mn$_{12}$ for $T \gtrsim 2$ K gives a good qualitatively agreement except for $H_z \approx 0$ as one can see comparing Figs. 3 and 4 with Figs. 6 and 7, respectively. For temperature $T \gtrsim 2$ K the discrepancy at $H_z \approx 0$ disappears as shown in Figs. 5 and 8. The quantitative agreement is not so good at the anticrossing fields. In any case the effect of the local fields should reduce and spread these resonances so that quite similar quantitative values might be found in both theories. According to GME results the experimental check of the spikes at the anticrossing fields on the actual compound Fe$_4$ should be easier at temperature lower than $T \simeq 0.6$ K.
APPENDIX A: STANDARD MASTER EQUATIONS (SME)

In this appendix we give the explicit form of the master equations (23) for Fe₄ (S = 5). The crystal field parameters are $B^0_3 = -0.216$, $B^0_4 = 1.16 \times 10^{-5}K$ and $g\mu_B/k_B = 1.34 K/T$. The eleven master equations are

\begin{align}
\dot{\rho}_{-5} &= W_{-5,-4}\rho_{-4} + W_{-5,-3}\rho_{-3} - (W_{-4,-5} + W_{-3,-5})\rho_{-5}, \\
\dot{\rho}_{-4} &= W_{-4,-5}\rho_{-5} + W_{-4,-3}\rho_{-3} + W_{-4,-2}\rho_{-2} - (W_{-5,-4} + W_{-3,-4} + W_{-2,-4})\rho_{-4}, \\
\dot{\rho}_{-3} &= W_{-3,-5}\rho_{-5} + W_{-3,-4}\rho_{-4} + W_{-3,-2}\rho_{-2} + W_{-3,-1}\rho_{-1} \\
&\quad - (W_{-5,-3} + W_{-4,-3} + W_{-2,-3} + W_{-1,-3})\rho_{-3}, \\
\dot{\rho}_{-2} &= W_{-2,-4}\rho_{-4} + W_{-2,-3}\rho_{-3} + W_{-2,-1}\rho_{-1} + W_{-2,0}\rho_{0} \\
&\quad - (W_{-4,-2} + W_{-3,-2} + W_{-1,-2} + W_{-0,-2})\rho_{-2}, \\
\dot{\rho}_{-1} &= W_{-1,-3}\rho_{-3} + W_{-1,-2}\rho_{-2} + W_{-1,0}\rho_{0} + W_{-1,1}\rho_{1} \\
&\quad - (W_{-3,-1} + W_{-2,-1} + W_{-0,-1} + W_{1,-1})\rho_{-1}, \\
\dot{\rho}_{0} &= W_{0,-2}\rho_{-2} + W_{0,-1}\rho_{-1} + W_{0,1}\rho_{1} + W_{0,2}\rho_{2} - (W_{-2,0} + W_{-1,0} + W_{1,0} + W_{2,0})\rho_{0}, \\
\dot{\rho}_{1} &= W_{1,-1}\rho_{-1} + W_{1,0}\rho_{0} + W_{1,2}\rho_{2} + W_{1,3}\rho_{3} - (W_{-1,1} + W_{0,1} + W_{2,1} + W_{3,1})\rho_{1}, \\
\dot{\rho}_{2} &= W_{2,0}\rho_{0} + W_{2,1}\rho_{1} + W_{2,3}\rho_{3} + W_{2,4}\rho_{4} - (W_{0,2} + W_{1,2} + W_{3,2} + W_{4,2})\rho_{2}, \\
\dot{\rho}_{3} &= W_{3,1}\rho_{1} + W_{3,2}\rho_{2} + W_{3,4}\rho_{4} + W_{3,5}\rho_{5} - (W_{1,3} + W_{2,3} + W_{4,3} + W_{5,3})\rho_{3}, \\
\dot{\rho}_{4} &= W_{4,2}\rho_{2} + W_{4,3}\rho_{3} + W_{4,5}\rho_{5} - (W_{2,4} + W_{3,4} + W_{5,4})\rho_{4}, \\
\dot{\rho}_{5} &= W_{5,3}\rho_{3} + W_{5,4}\rho_{4} - (W_{3,5} + W_{4,5})\rho_{5},
\end{align}

where

\begin{align}
W_{-5,-4} &= 1.62 \times 10^3 A(5.77 - 1.34H_z)^3 \left[1 + n \left(\frac{5.77 - 1.34H_z}{T}\right)\right] \\
W_{-5,-3} &= 180A(10.3 - 2.68H_z)^3 \left[1 + n \left(\frac{10.3 - 2.68H_z}{T}\right)\right] \\
W_{-4,-3} &= 1.76 \times 10^3 A(4.54 - 1.34H_z)^3 \left[1 + n \left(\frac{4.54 - 1.34H_z}{T}\right)\right]
\end{align}
\[ W_{-4,-2} = 432A(7.80 - 2.68H_z)^3 \left[ 1 + n \left( \frac{7.80 - 2.68H_z}{T} \right) \right] \tag{A15} \]

\[ W_{-3,-2} = 1.20 \times 10^3 A(3.26 - 1.34H_z)^3 \left[ 1 + n \left( \frac{3.26 - 1.34H_z}{T} \right) \right] \tag{A16} \]

\[ W_{-3,-1} = 672A(5.23 - 2.68H_z)^3 \left[ 1 + n \left( \frac{5.23 - 2.68H_z}{T} \right) \right] \tag{A17} \]

\[ W_{-2,-1} = 504A(1.97 - 1.34H_z)^3 \left[ 1 + n \left( \frac{1.97 - 1.34H_z}{T} \right) \right] \tag{A18} \]

\[ W_{-2,0} = 840A(2.63 - 2.68H_z)^3 \left[ 1 + n \left( \frac{2.63 - 2.68H_z}{T} \right) \right] \tag{A19} \]

\[ W_{-1,0} = 60A(0.658 - 1.34H_z)^3 \left[ 1 + n \left( \frac{0.658 - 1.34H_z}{T} \right) \right] \tag{A20} \]

\[ W_{1,-1} = 900A(2.68H_z)^3 \left[ 1 + n \left( \frac{2.68H_z}{T} \right) \right] \tag{A21} \]

with \( n(x) = [e^x - 1]^{-1} \), \( A = 1529 \) K^{-3} s^{-1}, \( T \) in Kelvin degrees and \( H_z \) in Tesla. \( W_{m,n} \) are obtained from \( W_{n,m} \) replacing \( 1 + n(x) \) by \( n(x) \) and \( W_{m,n} \) are obtained from \( W_{-m,-n} \) replacing \( H_z \) by \(-H_z\). The ansatz

\[ \rho_m(t) = \sum_{l=1}^{11} r_m^{(l)} e^{\lambda_l t} \tag{A22} \]

reduces the solution of the system of differential equations (23) to an eigenvalue problem

\[ W^{(0)} \cdot r' = \lambda_l r' \tag{A23} \]

where the non zero elements of the tridiagonal matrix \( W^{(0)} \) are given by

\[ W^{(0)}_{1,1} = -W_{-4,-5} - W_{-3,-5} \quad \text{,} \quad W^{(0)}_{1,2} = W_{-5,-4} \quad \text{,} \quad W^{(0)}_{1,3} = W_{-5,-3} \tag{A24} \]

\[ W^{(0)}_{2,1} = W_{-4,-5} \quad \text{,} \quad W^{(0)}_{2,2} = -W_{-5,-4} - W_{-3,-4} - W_{-2,-4} \]

\[ W^{(0)}_{2,3} = W_{-4,-3} \quad \text{,} \quad W^{(0)}_{2,4} = W_{-4,-2} \tag{A25} \]

\[ W^{(0)}_{3,1} = W_{-3,-5} \quad \text{,} \quad W^{(0)}_{3,2} = W_{-3,-4} \]

\[ W^{(0)}_{3,3} = -W_{-5,-3} - W_{-4,-3} - W_{-2,-3} - W_{-1,-3} \]

\[ W^{(0)}_{3,4} = W_{-3,-2} \quad \text{,} \quad W^{(0)}_{3,5} = W_{-3,-1} \tag{A26} \]
and the eigenvectors are column vectors given by $\mathbf{r}^l = (r_{-5}^l, r_{-4}^l, ..., r_{4}^l, r_{5}^l)$. Since $\sum_l W_{l,j}^{(0)} = 0$ for $j = 1, 2, ..., 11$, one of the eigenvalues, say $\lambda_{11}$, is zero.
APPENDIX B: GENERALIZED MASTER EQUATIONS (GME AND LLME)

To get the generalized master equation (GME) we account for the dominant quantum contributions coming from the transition probability rates neglected in the standard approach. As seen from Table I these contributions differ according to the magnetic field strength.

For $0 < H_z < 1T$ the dominant quantum contribution comes from $p(-5^*, 5^*)$ so that the only change concerns Eqs. (A1) and (A11) that become

$$
\dot{\rho}_{-5} = W_{-5^*, 5^*} \rho_5 + W_{-5, -4} \rho_{-4} + W_{-5, -5} \rho_{-5} - (W_{5^*, -5^*} + W_{-4, -5} + W_{-3, -5}) \rho_{-5},
$$

(B1)

$$
\dot{\rho}_5 = W_{5^*, -5^*} \rho_5 + W_{5^*, 5^*} \rho_5 + W_{5, 4} \rho_4 - (W_{5^*, 5^*} + W_{3, 5} + W_{4, 5}) \rho_5,
$$

(B2)

where

$$
W_{5^*, -5^*} = A \rho (5^*, 5^*) \left[ 1 + n \left( \frac{\epsilon_{-5^*} - \epsilon_{5^*}}{T} \right) \right],
$$

(B3)

and

$$
W_{-5^*, 5^*} = A \rho (5^*, 5^*) \left[ \frac{\epsilon_{-5^*} - \epsilon_{5^*}}{T} \right].
$$

(B4)

The solution of the system is reduced to the evaluation of the eigenvalues and eigenvectors of the matrix $W^{(1)}$ whose elements are the same as those of the matrix $W^{(0)}$ except

$$
W^{(1)}_{1,1} = -W_{-4, -5} - W_{-3, -5} - W_{5^*, -5^*}, \quad W^{(1)}_{1,11} = W_{-5^*, 5^*},
$$

(B5)

and

$$
W^{(1)}_{11,1} = W_{5^*, -5^*}, \quad W^{(1)}_{11,11} = -W_{3, 5} - W_{4, 5} - W_{5^*, 5^*}.
$$

(B6)

For $1 < H_z < 1.6T$ the dominant quantum contribution is $p(-5^*, 4^*)$; only Eqs. (A1) and (A10) are to be changed leading to the matrix $W^{(2)}$ which has the same elements as $W^{(0)}$ except

$$
W^{(2)}_{1,1} = -W_{-4, -5} - W_{-3, -5} - W_{4^*, -5^*}, \quad W^{(2)}_{1,10} = W_{-5^*, 4^*},
$$

(B7)

and

$$
W^{(2)}_{10,1} = W_{4^*, -5^*}, \quad W^{(2)}_{10,10} = -W_{2, 4} - W_{3, 4} - W_{5, 4} - W_{5^*, 4^*}.
$$

(B8)

For $1.6 < H_z < 2T$ the dominant quantum contribution is $p(-5^*, 3^*)$; only Eqs. (A1) and (A9) are to be changed leading to the matrix $W^{(3)}$ which has the same elements as $W^{(0)}$ except

$$
W^{(3)}_{1,1} = -W_{-4, -5} - W_{-3, -5} - W_{3^*, -5^*}, \quad W^{(3)}_{1,9} = W_{-5^*, 3^*}.
$$

(B9)
and
\[ W^{(3)}_{9,1} = W_{3^*, -5^*}, \quad W^{(3)}_{9,9} = -W_{1,3} - W_{2,3} - W_{4,3} - W_{5,3} - W_{-5^*, 3^*}. \] (B10)

For \( 2 < H_z < 2.75T \) the dominant quantum contribution is \( p(-5^*, 2^*) \); only Eqs. (A1) and (A8) are to be changed leading to the matrix \( W^{(4)} \) which has the same elements as \( W^{(0)} \) except
\[ W^{(4)}_{1,1} = -W_{-4, -5} - W_{-3, -5} - W_{2^*, -5^*}, \quad W^{(4)}_{1,8} = W_{-5^*, 2^*}. \] (B11)
and
\[ W^{(4)}_{8,1} = W_{2^*, -5^*}, \quad W^{(4)}_{8,8} = -W_{0,2} - W_{1,2} - W_{3,2} - W_{4,2} - W_{-5^*, 2^*}. \] (B12)

For \( 2.75 < H_z < 3 \ T \) the dominant quantum contribution is \( p(-5^*, 1^*) \); only Eqs. (A1) and (A7) are to be changed leading to the matrix \( W^{(5)} \) which has the same elements as \( W^{(0)} \) except
\[ W^{(5)}_{1,1} = -W_{-4, -5} - W_{-3, -5} - W_{1^*, -5^*}, \quad W^{(5)}_{1,7} = W_{-5^*, 1^*}. \] (B13)
and
\[ W^{(5)}_{7,1} = W_{1^*, -5^*}, \quad W^{(5)}_{7,7} = -W_{-1,1} - W_{0,1} - W_{2,1} - W_{3,1} - W_{-5^*, 1^*}. \] (B14)

Finally for \( H_z > 3 \ T \) the dominant quantum contribution is \( p(-5^*, 0^*) \); only Eqs. (A1) and (A6) are to be changed leading to the matrix \( W^{(6)} \) which has the same elements as \( W^{(0)} \) except
\[ W^{(6)}_{1,1} = -W_{-4, -5} - W_{-3, -5} - W_{0^*, -5^*}, \quad W^{(6)}_{1,6} = W_{-5^*, 0^*}. \] (B15)
and
\[ W^{(6)}_{6,1} = W_{0^*, -5^*}, \quad W^{(6)}_{6,6} = -W_{-2,0} - W_{-1,0} - W_{1,0} - W_{2,0} - W_{-5^*, 0^*}. \] (B16)

Since \( \sum_l W^{(n)}_{l,j} = 0 \) for \( j = 1, 2, \ldots, 11 \), one of the eigenvalues of each matrix \( W^{(n)} \) with \( n = 1, 2, \ldots, 6 \) is zero.

A different generalized master equation (LLME) was proposed by Leuenberger and Loss. They replace \( m^* \) by \( m \) in the phonon induced transition probability rate treating quantum tunneling in a pertubative way. In the LLME the differential equations for the diagonal and off-diagonal elements of the density matrix are
\[ \dot{\rho}_m = \frac{i}{\hbar} < m | [\rho, H_{el}] | m > + \sum_n W_{m,n} \rho_n - \rho_m \sum_n W_{n,m} \] (B17)
and
\[ \dot{\rho}_{m,m'} = \frac{i}{\hbar} < m | [\rho, \mathcal{H}_{\text{cf}}] | m' > - \frac{1}{2} \rho_{m,m'} \sum_n (W_{n,m} + W_{n,m'}). \] (B18)
respectively, with \( m, m' = -5, \ldots, 5 \) and \( m \neq m' \). The off-diagonal elements are originated from the choice of the eigenstates \( |m > \) that are not eigenstates of the crystal field Hamiltonian (1). The systems (B17) and (B18) have \( 2S + 1 = 11 \) and \( 2S(2S + 1) = 110 \) equations, respectively. This number is drastically reduced if one assumes\(^{10}\) that the crystal field Hamiltonian \( \mathcal{H}_{\text{cf}} \) may be replaced by its projection on the two-state system \( |m>, |m' > \) corresponding to the two levels of the diagonal part of the Hamiltonian that are degenerate at the anticrossing field \( H_{n}^{(0)} \). The elements of the projected Hamiltonian are
\[
\begin{align*}
<m | \mathcal{H}_{\text{cf}} | m > &= \epsilon_m (H_n^{(0)}) - g \mu_B m (H_z - H_n^{(0)}) \\
<m' | \mathcal{H}_{\text{cf}} | m > &= \epsilon_{m'} (H_n^{(0)}) \\
<m' | \mathcal{H}_{\text{cf}} | m' > &= \frac{1}{2} \Delta_{m,m'}^{(0)} (H_n^{(0)}) 
\end{align*}
\] (B19) (B20)
where \( \Delta_{m,m'}^{(0)} (H_n^{(0)}) \) is the splitting between levels \( \epsilon_m (H_n^{(0)}) = \epsilon_{m'} (H_n^{(0)}) \) at the anticrossing field. This splitting is to be evaluated by means of the time independent degenerate level perturbation theory pushed to a convenient order to give \( \Delta_{m,m'}^{(0)} \neq 0 \). For the tetrairon cluster Fe\(_4\) the perturbation Hamiltonian is \( V = B_2^2 O_2^2 + B_3^3 O_3^3 \). For \( m = -5 \) and \( m' = 5 \) (\( H_0^{(0)} = 0 \)) the chain formula\(^{9,10}\) for the splitting \( \Delta_{-5,5}^{(0)} \) is the sum of seven contributions: one corresponding to the chain formed by five potential \( B_2^2 O_2^2 \); the other six contributions coming from all permutations of two potentials \( B_2^2 O_2^2 \) and two potentials \( B_3^3 O_3^3 \). This gives \( \Delta_{-5,5}^{(0)} = 8.83 (B_2^2)^5 + 5.29 \times 10^3 (B_2^2)^3 (B_3^3)^2 = 5.12 \times 10^{-7} \) K. For \( m = -5 \) and \( m' = 4 \) (\( H_1^{(0)} = 0.478 \) T) one obtains \( \Delta_{-5,4}^{(0)} = 8.96 \times 10^2 (B_2^2)^3 B_3^3 + 9.21 \times 10^3 (B_3^3)^3 = 4.88 \times 10^{-6} \) K. For \( m = -5 \) and \( m' = 3 \) (\( H_2^{(0)} = 0.959 \) T) one obtains \( \Delta_{-5,3}^{(0)} = 53.9 (B_2^2)^4 + 7.33 \times 10^3 B_2^2 (B_3^3)^2 = 5.23 \times 10^{-5} \) K. For \( m = -5 \) and \( m' = 2 \) (\( H_3^{(0)} = 1.44 \) T) one has \( \Delta_{-5,2}^{(0)} = 1.59 \times 10^3 (B_2^2)^3 B_3^3 = 2.18 \times 10^{-4} \) K. For \( m = -5 \) and \( m' = 1 \) (\( H_4^{(0)} = 1.93 \) T) one has \( \Delta_{-5,1}^{(0)} = 98.2 (B_2^2)^3 + 1.57 \times 10^5 (B_3^3)^2 = 1.04 \times 10^{-3} \) K. For \( m = -5 \) and \( m' = 0 \) (\( H_5^{(0)} = 2.41 \) T) one has \( \Delta_{-5,0}^{(0)} = 1.24 \times 10^3 B_2^2 B_3^3 = 1.21 \times 10^{-2} \) K.

A quite similar result is obtained replacing the crystal field Hamiltonian by a two-level effective Hamiltonian\(^{4}\) \( \mathcal{H}_{\text{eff}} \) connecting only the two states that are mixed at the anticrossing field \( H_n \) that is
\[
\mathcal{H}_{\text{eff}} = \begin{pmatrix}
\epsilon_{-5}(H_n) + 5g \mu_B (H_z - H_n) & \frac{1}{2} \Delta_{-5,m}(H_n) \\
\frac{1}{2} \Delta_{-5,m}(H_n) & \epsilon_{m}(H_n) - m g \mu_B (H_z - H_n)
\end{pmatrix}
\] (B21)
where the energy splitting and anticrossing fields were taken from the diagonalization of the complete spin Hamiltonian. In particular, one obtains $\Delta_{-5,5}(0) = 5.03 \times 10^{-7}$ K for $H_z = 0; \Delta_{-5,4} = 1.46 \times 10^{-6}$ K for $H_1 = 0.477$ T; $\Delta_{-5,3} = 4.82 \times 10^{-5}$ K for $H_2 = 0.959$ T; $\Delta_{-5,2} = 2.18 \times 10^{-4}$ K for $H_3 = 1.44$ T; $\Delta_{-5,1} = 5.05 \times 10^{-4}$ K for $H_4 = 1.93$ T; $\Delta_{-5,0} = 1.21 \times 10^{-2}$ K for $H_5 = 2.41$ T. As one can see the agreement between these two approaches is very good as for the values of the anticrossing fields. Not so good is the agreement for the splittings even though the order of magnitude is recovered by the perturbation result. The overestimate is outstanding for $\Delta_{-5,4}$ and $\Delta_{-5,1}$. We use the effective Hamiltonian to write the LLME.

For magnetic field $H_z \approx 0$ the two-state subspace is spanned by $|-5>$ and $|5>$ so that Eqs. (B17) give

$$\dot{\rho}_{-5} = \frac{i}{2\hbar}\Delta_{-5,5}(\rho_{-5,5} - \rho_{5,-5}) + W_{-5,-4}\rho_{-4} + W_{-5,-3}\rho_{-3} - (W_{-4,-5} + W_{-3,-5})\rho_{-5}, \quad (B22)$$

$$\dot{\rho}_5 = \frac{i}{2\hbar}\Delta_{-5,5}(\rho_{5,-5} - \rho_{-5,5}) + W_{5,4}\rho_4 + W_{5,3}\rho_3 - (W_{4,5} + W_{3,5})\rho_5, \quad (B23)$$

while the equations for $\dot{\rho}_n$ with $n \neq -5,5$ are given by Eqs. (A2-A10). Analogously Eqs. (B18) give

$$\dot{\rho}_{5,-5} = \frac{i}{\hbar}(10g\mu_B H_z)\rho_{5,-5} + \frac{i}{2\hbar}\Delta_{-5,5}(\rho_5 - \rho_{-5})$$

$$- \frac{1}{2}(W_{3,5} + W_{4,5} + W_{-3,-5} + W_{-4,-5})\rho_{5,-5} \quad (B24)$$

and

$$\dot{\rho}_{-5,5} = -\frac{i}{\hbar}(10g\mu_B H_z)\rho_{-5,5} + \frac{i}{2\hbar}\Delta_{-5,5}(\rho_{-5} - \rho_5)$$

$$- \frac{1}{2}(W_{3,5} + W_{4,5} + W_{-3,-5} + W_{-4,-5})\rho_{-5,5}. \quad (B25)$$

Under the assumption$^{10}$ that the overall relaxation time is much longer than the time of decaying of the off-diagonal elements one can neglect their time dependence and take the solutions of Eqs. (B24) and (B25) for $\dot{\rho}_{-5,5} = \dot{\rho}_{5,-5} = 0$. So doing one obtains

$$\rho_{5,-5} = \frac{\frac{i}{2\hbar}\Delta_{-5,5}(\rho_5 - \rho_{-5})}{\frac{1}{2}(W_{3,5} + W_{4,5} + W_{-3,-5} + W_{-4,-5}) - \frac{i}{\hbar}(10g\mu_B H_z)} \quad (B26)$$

and $\rho_{-5,5}$ is the complex conjugate of $\rho_{5,-5}$. Replacing the off-diagonal terms so obtained in Eqs. (B22) and (B23) one obtains

$$\dot{\rho}_{-5} = \Gamma_{-5}^5 \rho_5 + W_{-5,-4}\rho_{-4} + W_{-5,-3}\rho_{-3} - (\Gamma_{-5}^5 + W_{-4,-5} + W_{-3,-5})\rho_{-5}, \quad (B27)$$

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and
\[ \dot{\rho}_5 = \Gamma_{-5}^5 \rho_{-5} + W_{5,4}\rho_4 + W_{5,3}\rho_3 - (\Gamma_{-5}^5 + W_{4,5} + W_{3,5})\rho_5. \]  

(B28)

where
\[ \Gamma_{-5}^5 = \left( \frac{\Delta_{-5,5}}{\hbar} \right)^2 \frac{W_{3,5} + W_{4,5} + W_{-3,-5} + W_{-4,-5}}{(W_{3,5} + W_{4,5} + W_{-3,-5} + W_{-4,-5})^2 + \left( \frac{2g\mu_B H_0}{\hbar} \right)^2} \]  

(B29)

Note that Eqs. (B27) and (B28) reduce to Eqs. (B1) and (B2) if one replaces both \( W_{-5^*,5^*} \) and \( W_{5^*,-5^*} \) by \( \Gamma_{-5}^5 \). In this way we obtain directly from Eqs. (B5) and (B6) the new matrix \( W^{(1)} \) and use the same procedure illustrated in the Appendix A to find the relaxation time.

For \( H_z \approx H_1 \) the crystal field Hamiltonian is projected on the two-state subspace \( |-5> \), \( |4> \) and we obtain the new matrix \( W^{(2)} \) replacing both \( W_{-5^*,4^*} \) and \( W_{4^*,-5^*} \) in Eqs. (B7) and (B8) by \( \Gamma_{-5}^4 \) where
\[ \Gamma_{-5}^4 = \left( \frac{\Delta_{-5,4}}{\hbar} \right)^2 \frac{W_{2,4} + W_{3,4} + W_{5,4} + W_{-3,-5} + W_{-4,-5}}{(W_{2,4} + W_{3,4} + W_{5,4} + W_{-3,-5} + W_{-4,-5})^2 + \left( \frac{16g\mu_B (H_z - H_1)}{\hbar} \right)^2}. \]  

(B30)

For \( H_z \approx H_2 \) the new matrix \( W^{(3)} \) is obtained replacing both \( W_{-5^*,3^*} \) and \( W_{3^*,-5^*} \) in Eqs. (B9) and (B10) by \( \Gamma_{-5}^3 \) where
\[ \Gamma_{-5}^3 = \left( \frac{\Delta_{-5,3}}{\hbar} \right)^2 \frac{W_{1,3} + W_{2,3} + W_{4,3} + W_{5,3} + W_{-3,-5} + W_{-4,-5}}{(W_{1,3} + W_{2,3} + W_{4,3} + W_{5,3} + W_{-3,-5} + W_{-4,-5})^2 + \left( \frac{16g\mu_B (H_z - H_2)}{\hbar} \right)^2}. \]  

(B31)

For \( H_z \approx H_3 \) the new matrix \( W^{(4)} \) is obtained replacing both \( W_{-5^*,2^*} \) and \( W_{2^*,-5^*} \) in Eqs. (B11) and (B12) by \( \Gamma_{-5}^2 \) where
\[ \Gamma_{-5}^2 = \left( \frac{\Delta_{-5,2}}{\hbar} \right)^2 \frac{W_{0,2} + W_{1,2} + W_{3,2} + W_{4,2} + W_{-3,-5} + W_{-4,-5}}{(W_{0,2} + W_{1,2} + W_{3,2} + W_{4,2} + W_{-3,-5} + W_{-4,-5})^2 + \left( \frac{16g\mu_B (H_z - H_3)}{\hbar} \right)^2}. \]  

(B32)

For \( H_z \approx H_4 \) the new matrix \( W^{(5)} \) is obtained replacing both \( W_{-5^*,1^*} \) and \( W_{1^*,-5^*} \) in Eqs. (B13) and (B14) by \( \Gamma_{-5}^1 \) where
\[ \Gamma_{-5}^1 = \left( \frac{\Delta_{-5,1}}{\hbar} \right)^2 \frac{W_{-1,1} + W_{0,1} + W_{2,1} + W_{3,1} + W_{-3,-5} + W_{-4,-5}}{(W_{-1,1} + W_{0,1} + W_{2,1} + W_{3,1} + W_{-3,-5} + W_{-4,-5})^2 + \left( \frac{12g\mu_B (H_z - H_4)}{\hbar} \right)^2}. \]  

(B33)
For $H_z \approx H_5$ the new matrix $\overline{W}^{(6)}$ is obtained replacing both $W_{-5,0}^*$ and $W_{0,-5}^*$ in Eqs. (B15) and (B16) by $\Gamma_{-5}^0$ where

$$
\Gamma_{-5}^0 = \left( \frac{\Delta_{-5,0}}{\hbar} \right)^2 \frac{W_{-2,0}^* + W_{-1,0}^* + W_{1,0}^* + W_{2,0}^* + W_{-3,-5}^* + W_{-4,-5}^*}{(W_{-1,1}^* + W_{0,1}^* + W_{2,1}^* + W_{3,1}^* + W_{-3,-5}^* + W_{-4,-5}^*)^2 + \left[ \frac{10g\mu_B(H_z-H_5)}{\hbar} \right]^2}.
$$

(B34)