Phonoemissive Spin Tunneling in Molecular Nanomagnets

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A new mechanism is proposed for the magnetization reversal of molecular nanomagnets such as Fe$_8$. In this process the spin tunnels from the lowest state near one easy direction to the first excited state near the opposite easy direction, and subsequently decays to the second easy direction with the emission of a phonon, or it first emits a phonon and then tunnels to the final state. This mechanism is the simplest imaginable one that allows magnetization relaxation in the presence of a longitudinal magnetic field that is so large that the nuclear spin environment cannot absorb the energy required for energy conservation to hold. It is proposed as a way of understanding both magnetization relaxation and Landau-Zener-Stückelberg experiments. The requisite Fermi golden rule rate, and the spin-flip rates are calculated, and it is found that these rates are much too low by several orders of magnitude. Thus the understanding of magnetic relaxation in the experiments remains an open question.

1 Introduction and Background

Over the last fifteen years or so, molecular nanomagnets (also known as single-molecule magnets, or molecular magnets) have provided us with an entirely new class of magnetic systems, showing many novel phenomena not seen previously [1]. Among the most dramatic of these is the observation of gap oscillations wherein the tunnel splitting between the two lowest energy states on opposite sides of an energy barrier oscillates as a function of a static magnetic field applied along the hard axis of the molecule [2]. Although many aspects of this phenomenon can be understood by considering the idealized problem of an isolated molecule, a full understanding of the experimental procedures and results presents several complexities and puzzles. It is the purpose of this paper to address one of these puzzles. To keep the discussion focussed and free of lapidary generalizations, we will consider the example of the Fe$_8$ molecule in this paper, but the central ideas are applicable more broadly.

To understand the basic phenomenon at issue, let us first consider one Fe$_8$ molecule in the solid, and ignore its interaction with other molecules and any other environmental degree of freedom. The molecule has spin 10 in its ground manifold. At low temperatures only the spin degree of freedom has any life in it, and all others are frozen. This degree of freedom is governed by an anisotropy Hamiltonian

$$\mathcal{H}_a = k_1 S_z^2 + k_2 S_y^2 + \mathcal{H}_4 - g \mu_B S \cdot \mathbf{H},$$

where $\mathbf{S}$ is a dimensionless spin operator (of magnitude $S$, equal to 10 for Fe$_8$), $k_1 > k_2 > 0$ are anisotropy coefficients, $g$ is a g-factor (equal to 2 for Fe$_8$), and $\mathbf{H}$ is an external magnetic field. The term $\mathcal{H}_4$ is of fourth order in the components of $\mathbf{S}$, and while it is responsible for surprising and important features in the tunneling spectrum, we do not show it explicitly because we will not need to discuss those aspects in this paper.

When $\mathbf{H} = 0$, Eq. (1) has two ground states corresponding (classically speaking) to $S_z = \pm 10$, or $m = \pm 10$, where $m$ is the $S_z$ or Zeeman quantum number. These two states are degenerate, and mixed by tunneling, as shown in Fig. 1. If we now turn on $\mathbf{H}||\hat{x}$, the new classical ground states are still degenerate, but

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Fig. 1 Schematic energy level diagram of Fe₈ showing (a) the basic tunneling process between ground levels, and (b) the phonoemissive process, in which the molecule tunnels from \( m = -10 \) to an intermediate virtual state \( m = 9 \), and then makes a transition to \( m = 10 \) with the emission of a phonon (as shown by the dot-dashed line). Or, the phonon can be emitted first accompanying a transition to the \( m = -9 \) state, followed by tunneling to the \( m = 10 \) state. This process appears to be the simplest way in which the magnetization can relax when the bias \( \epsilon \) is much greater than \( W \), the effective width of the levels induced by the nuclear spin environment. Direct tunneling in this case would not conserve energy, and the nuclear spins are incapable of absorbing an energy much greater than \( W \).

the tunnel splitting between them (\( \Delta_{-10,10} \equiv \Delta \)) does not increase monotonically with \( H_x \). Instead it oscillates as shown in Fig. 2. This oscillation is best understood in terms of instanton [3,4,5], but readers unfamiliar with instantons may regard it as an outcome of direct diagonalization of the Hamiltonian [1]. Similarly, if a magnetic field is applied along the \( z \) axis so as to bring the \( m = -10 \) and \( m = 9 \) states into resonance, the system will be able to tunnel between these states. This tunnel splitting (\( \Delta_{-10,9} \equiv \Delta' \)) also oscillates as a function of an additional field \( H_x \) along the hard axis. The same holds for tunneling between \( m = -10 \) and \( m = 8 \), and other pairs of states. By symmetry, if the \( z \) axis field is such to bring the \( m = -9 \) and \( m = 10 \) states into resonance, the splitting \( \Delta_{-9,10} \) will be the same as \( \Delta_{-10,9} \).

Fig. 2 The gap oscillations in Fe₈. Part (a), kindly supplied by Dr. Wernsdorfer, shows data from Ref. [2]. The curve labeled \( n = 0 \) is the \(-10 \rightarrow 10\) tunneling, that labeled \( n = 1 \) is the \(-10 \rightarrow 9\) tunneling, and so on. Part (b) shows a fit to data for the tunnel splitting between the lowest pair of levels, taken from Ref. [12].

(To avoid misunderstanding, we note that when we speak of the state with \( m = -10 \), say, we do not literally mean the eigenstate of \( S_z \) with eigenvalue \(-10\). Rather, we mean the eigenstate of \( \mathcal{H}_n \) (ignoring tunneling) that maps on to the \( S_z = -10 \) state in the following way. We imagine subtracting a zeroth order
Hamiltonian \((k_1 + k_2)(S_z^2 + S_{z'}^2)/2\) from Eq. (1), and treating the result as a perturbation. The state that we are talking about is then the one that would develop from the \(S_z = -10\) state by low order perturbation theory. It would perhaps be better to use a notation such as \(m^*\) for the perturbed state, but as long as this qualification is understood, there is little benefit from doing so.)

If an Fe\(_8\) molecule really did not interact with the rest of the world, the tunneling described above would lead to coherent flip-flop as in the inversion resonance of ammonia. No such flip-flop is seen, and indeed that is to be expected. Any environmental degree of freedom which couples to the magnetic moment of the molecule will tend to suppress quantum coherence, and for resonance between states with such a large difference in their magnetic moments, one would expect that all vestiges of coherence are destroyed. This is indeed so, and one finds that because of the nuclear spin environment, transitions between the \(\pm S\) states are totally incoherent, and one finds a transition probability per unit time given by \(p_{\text{LZS}} = 1 - \exp \left(-\frac{\pi \Delta^2}{2h |\dot{\epsilon}|}\right)\).

Here, \(W \approx 10E_{dn}\), where \(E_{dn}\) is the energy of dipole-dipole interaction between the molecular electronic spin and the nuclear spins of nearby nonmagnetic atoms such as N and H which are always present in the molecules studied, and \(\epsilon\) is the bias, or the energy of the \(m = -S\) state relative to the \(m = S\) state. This bias can arise from an externally applied field along the \(z\) axis, or from the dipole field created by other molecules in the sample. Indeed, it is found that this dipole field is of order 100 Oe \([3,2]\), so the bias is of order 0.1 K. By comparison, \(E_{dn} \sim 1\) mK.

Given that \(\epsilon \gg W\) for most molecules in any solid sample, the spins of most molecules are frozen, in that they do not even undergo incoherent tunneling. To overcome this problem, the authors of Ref. \([2]\) use the ingenious idea of sweeping through the resonance by applying a time-dependent longitudinal (\(z\) axis) magnetic field as shown in Fig. 3. This is the Landau-Zener-Stückelberg (LZS) protocol \([10]\). The molecule flips from \(m = -10\) to \(m = 10\) (or vice versa) with a probability

\[
p_{\text{LZS}} = 1 - \exp \left(-\frac{\pi \Delta^2}{2h |\dot{\epsilon}|}\right)
\]

for every sweep through the crossing. Here \(\dot{\epsilon}\) is the rate at which the bias changes. For transitions between \(m = \pm S, |\dot{\epsilon}| = 4\mu B S|dH_z/dt|, since \(g = 2\). It is found that for \(H_z\) between \(\sim 3\) mT/s and \(1\) T/s, the LZS formula is obeyed, allowing one to extract \(\Delta\) from a measurement of \(p_{\text{LZS}}\).

![Fig. 3](image)

**Fig. 3** The Landau-Zener-Stückelberg protocol. In part (a) we show the direct LZS mechanism, in which the energy levels of the \(m = \pm 10\) states are swept by applying a time-dependent field along the \(z\) axis. In (b) we show the same process when the final state also contains a phonon.

At this point it should be stated that the LZS formula \([3]\) only holds for coherent transitions. For incoherent transitions, a different formula, due to Kayanuma \([11]\) is better:

\[
p_K = \frac{1}{2} \left[1 - \exp \left(-\frac{\pi \Delta^2}{h |\dot{\epsilon}|}\right)\right].
\]
Remarkably, for fast sweeps, i.e., when $|\epsilon| \gg \Delta^2/\hbar$, both formulas agree:

$$p_{\text{LZS}} = p_k = \frac{\pi \Delta^2}{2\hbar |\epsilon|}, \quad (|\epsilon| \gg \Delta^2/\hbar)$$

(5)

Experimentally, the LZS formula starts to fail for $dH_z/dt \lesssim 3$ mT/s (the Kayanuma formula is not precisely obeyed either), but if one only employs it for fast sweeps, then the details of the decoherence do not matter, and the extraction of $\Delta$ is reliable.

2 The Phonoemissive Tunneling Process

We are now ready to describe the puzzle mentioned at the start of Sec. 1. Theoretically, at the minima, $\Delta$ vanishes strictly. Experimentally, this is not so. In Ref. [12], this was explained by arguing that every molecule sat in a nonzero transverse magnetic field created by the other molecules that acts in addition to the applied $H_z$. Thus $\Delta \neq 0$ for any molecule, and the measured $\Delta$ should really be found by taking an average over the inhomogeneous spread in $H_z$ of order 100 Oe. (Actually, the quantity that should be averaged is $\Delta^2$.) In addition, the experimental data show that the inferred values of $\Delta$ at the minima grow linearly with $H_z$. To explain this, it was assumed that there was a small degree of misalignment of the magnetic axes of the molecules (of order $\sigma_\theta \sim 1$–2°) because of various types of defects in the material, which is rather soft and organic. This means that there is a small nonzero field $H_{\text{med}} \simeq H_z \sigma_\theta$ along the local medium axis of each molecule, and since for an isolated molecule $\Delta \propto H_{\text{med}}$ in the vicinity of one of the minima, the measured $\Delta$ would pick up a contribution linear in $H_z$.

As can be seen from Fig. 2(b), the fit between the theory based on these assumptions and the experimental data is good; indeed it is rather too good. For while the first assumption—of an inhomogeneous transverse dipolar field—is well justified and hardly an assumption, the second—of misalignment of the magnetic axes—is somewhat ad hoc. We have therefore sought another way in which the spin could flip for which the rate has an $H_z$ dependence. The mechanism we propose is shown in Fig. 1(b). It involves a virtual tunneling transition from the $m = -10$ to the $m = 9$ state, followed by a transition from the $m = 9$ state to the $m = 10$ state with the emission of a phonon. Alternatively, we could first make a virtual transition to the $m = 9$ state accompanied by the emission of a phonon, and then tunnel to the $m = 10$ state. Either way, the final state is the same, i.e., the spin is in the $m = 10$ state, and a phonon has been emitted. We refer to this as phonoemissive tunneling. The reverse process, involving the absorption of a phonon, will also take place if $k_B T > \epsilon$, for then phonons of energy $\epsilon$ will be available to be absorbed. In this paper we work only at $T = 0$, so only the emission process takes place. The generalization to $T \neq 0$ is straightforward.

At this point it may be useful to clarify that the $-10 \rightarrow 9$ (or $-9 \rightarrow 10$) tunneling transition is possible even if the levels are not in resonance. This transition would have very small probability if we were thinking of the $m = 9$ state as a true final state (not to mention that it would require some environmental degree of freedom to supply the energy necessary for energy conservation), but we are only exploiting $m = 9$ as a virtual intermediate state. For the virtual process, there is always a matrix element of the Hamiltonian, or tunneling amplitude, equal to $-i\Delta'/2\hbar$ per unit time. Indeed, for $\text{Fe}_8$, $\Delta'$ as a function of $H_z$ is maximal when $\Delta$ is minimal.

The process just described could also be germane to experimental situations other than LZS. Consider, for example, magnetic relaxation without any swept field. If, for a given molecule, $\epsilon \gg W$ for some reason, the rate (2) is very small, and phonoemissive tunneling may be important. Indeed, we shall calculate the second order Fermi golden rule rate for this situation first, in Sec. 3, before considering the LZS protocol in Sec. 4. The process could also be important for ultraslow LZS sweeps, and for inverse LZS sweeps [13].

The second step of phonoemissive tunneling is governed by the spin-phonon Hamiltonian,

$$\mathcal{H}_{\text{sp}} = D_{ijkl} u_{ij}^{\text{op}} \{S_k, S_l\}.$$  (6)
Here, $u_{ij}^{op}$ is the operator for the strain tensor, $D_{ijkl}$ is the magnetoelastic tensor, $\{,\}$ denotes the anticommutator, and there is an implicit sum over the Cartesian indices $i$, $j$, $k$, and $l$. The tensor $D_{ijkl}$ is not well known for Fe$_8$, so we shall simplify Eq. (7) to

$$\mathcal{H}_{sp} = D u_{ij}^{op} \{S_i, S_j\}. \quad (7)$$

The quantity $D$ has dimensions of energy, and may be taken to be of the same order of magnitude as the anisotropy coefficients $k_1$ and $k_2$. The strain tensor is given by

$$u_{ij}^{op} = \frac{1}{2} \left( \frac{\partial u_{ij}^{op}}{\partial x_j} + \frac{\partial u_{ij}^{op}}{\partial x_i} \right), \quad (8)$$

where $u^{op}(x)$ is the displacement field operator given by

$$u^{op}(x) = \sum_\alpha \sqrt{\frac{\hbar}{2MN\omega_\alpha}} (a_\alpha e^{i\mathbf{q}_\alpha \cdot \mathbf{x}} + h.c.). \quad (9)$$

Here, $a_\alpha$ and $a_\alpha^\dagger$ are the destruction and creation operators for phonons of mode $\alpha$, $\mathbf{q}_\alpha$, $\omega_\alpha$, and $e_\alpha$ are the wavevector, frequency, and polarization vector for this mode, $M$ is the mass of all atoms in a unit cell, and $N$ is the number of unit cells in the crystal. In writing Eq. (9), we have kept only long wavelength phonon modes, for which relative motion of the atoms in a unit cell is negligible, and this is why the total unit cell mass $M$ appears. These are the only modes relevant for low temperatures and low energy processes. We can also take the polarization vectors to be real for them.

For the $m = 9$ to $m = 10$ transition, the only nonzero matrix elements arise from the spin operators $\{S_x, S_z\}$ and $\{S_y, S_z\}$. We have

$$\langle m = S | \{S_x, S_z\} | m = S - 1 \rangle = (S - \frac{1}{2})\sqrt{2S} \equiv A,$$

$$\langle m = S | \{S_y, S_z\} | m = S - 1 \rangle = -i(S - \frac{1}{2})\sqrt{2S} = -iA. \quad (10)$$

It is now apparent that we could also take an $m = 8$ intermediate state, since the operator $\{S_x, S_y\}$ would yield a non zero matrix element, and there is a nonzero amplitude to tunnel from $m = -10$ to $m = 8$. We will not give formulas for this case explicitly, as the requisite modifications are straightforward. Other intermediate states are much less important, since they would involve multiphonon processes with far smaller probabilities.

### 3 Fermi Golden Rule

We now calculate the rate for phonoemissive tunnelling when there is no swept field. We denote the initial, intermediate (or virtual), and final states by $|i\rangle$, $|v\rangle$, and $|\alpha\rangle$, where,

$$|i\rangle = |m = -10, \text{no phonons}\rangle, \quad (11)$$

$$|v\rangle = |m = 9, \text{no phonons}\rangle, \quad (12)$$

$$|\alpha\rangle = |m = 10, \text{one phonon in mode } \alpha\rangle. \quad (13)$$

The energies of these states are

$$E_i = \epsilon_{-10}, \quad E_v = \epsilon_9, \quad E_\alpha = \epsilon_{10} + \hbar\omega_\alpha, \quad (14)$$

where $\epsilon_m$ is the energy of the molecular spin alone. Alternatively, the transition could take place through a different virtual intermediate state,

$$|v\rangle = |m = -9, \text{one phonon in mode } \alpha\rangle. \quad (15)$$
in which case,
\[
E_v = \epsilon_{-9} + \hbar \omega_\alpha. \tag{16}
\]
The transition rate is given by the second order Fermi golden rule,
\[
\Gamma_{pet} = \frac{2\pi}{\hbar} \sum_\alpha |V_{\alpha i}^{(2)}|^2 \delta(E_i - E_{\alpha}), \tag{17}
\]
where
\[
V_{\alpha i}^{(2)} = \sum_v \frac{\langle \alpha | H_{sp} | v \rangle \langle v | H_s | i \rangle}{E_i - E_v}. \tag{18}
\]
It should be noted that the sum over virtual states in Eq. (18) does not entail a sum over the phonon modes; rather it is performed for a particular mode \( \alpha \). The sum over phonon modes is performed in Eq. (17).

It is evident that because of symmetry, the two contributions to Eq. (18) differ only in the energy denominators. We shall assume that the bias \( \epsilon \) is small in comparison with the energy difference
\[
E_{ex} \equiv \epsilon_{9} - \epsilon_{10}. \tag{19}
\]
In that case, both energy denominators may be replaced by \(-E_{ex}\). We need only do the calculation for the intermediate state (12), and double the answer to get \( V^{(2)} \). Further, it is more accurate to calculate the energy difference using the results for \( \epsilon_m \) when \( H_z = 0 \).

The actual calculation is straightforward. Consider the intermediate state (12). For the matrix element of \( H_s \) we have
\[
\langle v | H_s | i \rangle = \Delta'/2. \tag{20}
\]
Next let us examine the matrix element of \( H_{sp} \). Consider the strain field \( u_{xz}^{op} \). We have
\[
u_{xz}^{op} = \frac{i}{2} \sum_\alpha \sqrt{\frac{\hbar}{2MN\omega_\alpha}} (a_\alpha - a_\alpha^\dagger)(e_{\alpha,x}q_{\alpha,z} + e_{\alpha,z}q_{\alpha,x}). \tag{21}
\]
When we take the matrix element of this operator, we are left with the c-number
\[
u_{xz}^{a} = -\frac{i}{2} \sqrt{\frac{\hbar}{2MN\omega_\alpha}} (e_{\alpha,x}q_{\alpha,z} + e_{\alpha,z}q_{\alpha,x}). \tag{22}
\]
Similarly, from \( u_{yz}^{op} \) we get \( u_{yz}^{a} \), which is the same expression with the index \( x \) replaced by \( y \) everywhere. The matrix elements of the spin parts of \( H_{sp} \) have already been found in Eq. (10). Hence, doubling the result as explained above to account for the two intermediate states, we get
\[
V_{\alpha i}^{(2)} = -\frac{AD\Delta'}{E_{ex}}(u_{xz}^{\alpha} - iu_{yz}^{\alpha}). \tag{23}
\]
Therefore,
\[
\Gamma_{pet} = \frac{2\pi}{\hbar} \left( \frac{AD\Delta'}{E_{ex}} \right)^2 \sum_\alpha |(u_{xz}^{\alpha} - iu_{yz}^{\alpha})|^2 \delta(\hbar \omega_\alpha - E_{if}), \tag{24}
\]
where
\[
E_{if} = \epsilon_{-10} - \epsilon_{10} = \epsilon. \tag{25}
\]
Since \( \omega_\alpha > 0 \), the rate is nonzero only if \( \epsilon > 0 \), i.e., if energy conservation requires the emission of phonons. To perform the sum over phonon modes, we replace the mode index \( \alpha \) by the pair \((q, s)\), where \( q \) is the wavevector, and \( s (= 1, 2, \text{or} 3) \) labels the three acoustic modes. The sum over \( q \) can be turned into an integral in the usual way, and we get

\[
\Gamma_{\text{pet}} = \frac{2\pi}{\hbar} \left( \frac{AD\Delta'}{E_{\text{ex}}} \right)^2 \frac{h v_0}{8M} \int \frac{d^3 q}{(2\pi)^3} \omega_q \frac{1}{\omega_q} \left[ (e_{s,x}q_z + e_{s,z}q_x)^2 + (e_{s,y}q_z + e_{s,z}q_y)^2 \right] \delta(h\omega_q - \epsilon),
\]

where \( v_0 \) is the volume of a unit cell. It should be remembered that \( e_s \) depends on \( q \).

To proceed further and obtain an order of magnitude estimate, we make the simplifying assumption that the material is isotropic, so that for any \( q \), there is one longitudinal mode and two (degenerate) transverse modes, and that \( \omega_q \) is either \( c_L q \) or \( c_T q \), where \( c_L \) and \( c_T \) are the longitudinal and transverse sound velocities. The integral and sum over \( q \) and \( s \) are then elementary, and we get

\[
\Gamma_{\text{pet}} = \frac{1}{5\pi} \left( \frac{AD\Delta'}{E_{\text{ex}}} \right)^2 \left( \frac{1}{c_T^3} + \frac{1}{3c_L^3} \right) \frac{e^3}{\rho h^4},
\]

where

\[
\rho = M/v_0
\]

is the mass density of the material. The \( e^3 \) dependence of the rate (27) is characteristic of other rates involving phonon emission, and the \( A^2 \sim S^3 \) factor has the same origin as in Ref [14]. Since \( c_T \sim c_L/2 \), the transverse sound term is likely to dominate in Eq. (27).

### 4 The Landau-Zener-Stückelberg Rate

Next, let us consider how the phonoemissive process affects the spin-flip probability if the longitudinal field is swept in a LZS protocol. The role of \( \Delta \) in Eq. (2) is now played by the second-order matrix element \( V_{\alpha i}^{(2)} \). We will only consider the limit of fast sweep, in which case the answer may be found by a perturbative expansion in \( V_{\alpha i}^{(2)} \). At the same time, it should be noted that the sweep is slow on the time scale \( h/E_{\text{ex}} \) required to establish the underlying second-order process.

With the same notation as in Sec. 3, the time-dependent Hamiltonian for the LZS protocol may be written as

\[
\mathcal{H}_{\text{LZS}} = E_i(t)|i\rangle\langle i| + \sum_{\alpha} E_{\alpha}(t)|\alpha\rangle\langle \alpha| + \sum_{\alpha} \left[V_{\alpha i}^{(2)}|i\rangle\langle \alpha| + \text{h.c.}\right],
\]

where

\[
E_i(t) = \epsilon_{-10} + g\mu_B S \hat{H}_z t, \quad E_{\alpha}(t) = \epsilon_{10} + \hbar \omega_\alpha - g\mu_B S \hat{H}_z t.
\]

Hence,

\[
\dot{\epsilon} = 2g\mu_B \dot{\hat{H}}_z.
\]

Further, the energies \( \epsilon_{\pm 10} \) of a single molecule are now the eigenvalues of \( \mathcal{H}_s \) with \( \mathbf{H} = 0 \). It follows that that these energies are equal, and we may take them as our reference level:

\[
\epsilon_{10} = \epsilon_{-10} = 0.
\]
In an interaction picture, the time-dependent state of the system can be written as
\[ |\psi(t)\rangle = a(t)e^{-i\frac{\epsilon t^2}{2\hbar}}|i\rangle + \sum_{\alpha} b_{\alpha}(t)e^{-i[\omega_{\alpha} t - i\epsilon t^2/2\hbar]}|\alpha\rangle. \] (34)

Feeding this form into the Schrödinger equation, we obtain the equations of motion for the amplitudes \(a(t)\) and \(b_{\alpha}(t)\):
\[ \dot{a} = -i\frac{\hbar}{\bar{h}} \sum_{\alpha} V_{\alpha}^{(2)} b_{\alpha}(t) e^{-i[\omega_{\alpha} t - i\epsilon t^2/2\hbar]}, \]
\[ \dot{b}_{\alpha} = -i\frac{\hbar}{\bar{h}} V_{\alpha}^{(2)} a(t) e^{i[\omega_{\alpha} t - i\epsilon t^2/2\hbar]}. \] (35)

We wish to solve these equations with the initial conditions
\[ |a(-\infty)\rangle = 1, \quad b_{\alpha}(-\infty) = 0. \] (36)

Following Kayanuma [11], the solution may be obtained as a power series in \(V^{(2)}\) by iteratively substituting Eqs. (35) into one another. For us it suffices to take only the first order answer, so we put \(a(t) = 1\) in the second equation, which can then be integrated to yield
\[ b_{\alpha}(t) \approx -i\frac{\hbar}{\bar{h}} V_{\alpha}^{(2)} \int_{-\infty}^{t} dt_1 e^{i[\omega_{\alpha} t_1 - i\epsilon t_1^2/2\hbar]}. \] (37)

Thus, ignoring a unimodular multiplicative factor,
\[ b_{\alpha}(\infty) = \frac{i}{\bar{h}} V_{\alpha}^{(2)} \sqrt{\frac{2\pi \hbar}{i\epsilon}}. \] (38)

The net spin-flip probability is
\[ p_{LZS}^{(2)} = \sum_{\alpha} |b_{\alpha}(\infty)|^2 \] (39)

The sum over phonon modes is performed in the same way as in Sec. 3, except that since there is no delta function of energy in the summand, one must cut the sum off in some way. The natural cutoff is provided by the peak value of the bias between the \(m = \pm 10\) states due to the swing in the longitudinal field. Writing this swing as \(H_{ac}\), we define
\[ E_{ac} = g\mu_B S H_{ac}. \] (40)

We then find
\[ p_{LZS}^{(2)} = \frac{1}{10\pi} \left( \frac{AD\Delta’}{E_{ex}} \right)^2 \left( \frac{1}{c_T^2} + \frac{1}{3c_L^2} \right) \frac{E_{ac}^4}{\rho h^3 \epsilon}. \] (41)

The indirect flip probability must be added to the direct process result (5). The result can then be cast in the same form as Eq. (5) itself, provided we replace \(\Delta\) by an effective splitting \(\Delta_{eff}\), where
\[ \Delta_{eff}^2 = \Delta^2 + \Delta’^2 \left[ \frac{1}{5\pi^2} \left( \frac{AD}{E_{ex}} \right)^2 \left( \frac{1}{c_T^2} + \frac{1}{3c_L^2} \right) \frac{E_{ac}^4}{\rho h^3 \epsilon} \right]. \] (42)

The term in square brackets provides a quick way to see the relative importance of the phonoemissive process. If we take \(H_{ac} = 100\) Oe, then \(E_{ac}/\hbar = 1.8 \times 10^{13}\) sec\(^{-1}\). We may take \(D = 0.25\) K, and \(E_{ex} = 5\) K as reasonable estimates. For the sound speeds and density, we may take representative values
for common organic materials. For paraffin wax, for example, \( \rho = 0.91 \, \text{g/cm}^3 \), \( c_L = 1.94 \times 10^5 \, \text{cm/s} \), and we have not been able to find a value for \( c_T \). For polyethylene, \( \rho = 0.90 \, \text{g/cm}^3 \), \( c_L = 1.95 \times 10^5 \, \text{cm/s} \), and \( c_T = 0.54 \times 10^5 \, \text{cm/s} \), and for polystyrene, \( \rho = 1.06 \, \text{g/cm}^3 \), \( c_L = 2.35 \times 10^5 \, \text{cm/s} \), and \( c_T = 1.12 \times 10^5 \, \text{cm/s} \). Hence we take \( \rho = 1 \, \text{g/cm}^3 \), and \( c_T = 10^5 \, \text{cm/s} \). The term in square brackets is then of order \( 10^{-12} \), which is disappointingly small. Even if we take \( \Delta' \approx 100\Delta \) as is appropriate if the intermediate state is \( m = \pm 8 \) in Fe\(_8\), the contribution of the phonoemissive process is negligible. Nevertheless, the process remains the simplest imaginable candidate for the magnetization relaxation mechanism. To this author’s mind, it remains an urgent problem to resolve this puzzle.

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References

[1] D. Gatteschi, R. Sessoli, and J. Villain, *Molecular Nanomagnets* (Oxford University Press, Oxford, 2006). This book gives a comprehensive and authoritative review of the entire field of SMM’s. The LZS process and the problem of relaxation are mainly discussed in Chapters 8 and 9, and many more references to related work may be found therein.

[2] W. Wernsdorfer and R. Sessoli, Science 284, 133 (1999).

[3] D. Loss, D. P. DiVincenzo, and G. Grinstein, Phys. Rev. Lett. 69, 3232 (1992).

[4] J. von Delft and C. L. Henley, Phys. Rev. Lett. 69, 3236 (1992).

[5] A. Garg, Europhys. Lett. 22, 205 (1993).

[6] N. V. Prokofev and P. Stamp, Phys. Rev. Lett. 80, 5794 (1998); J. Low. Temp. Phys. 113, 1147 (1998).

[7] A. Vijayaraghavan and A. Garg, Phys. Rev. B 79, 104423 (2009).

[8] T. Ohm, C. Sangregorio, C. Paulsen, Euro. Phys. J. B 6, 195 (1998).

[9] W. Wernsdorfer, T. Ohm, C. Sangregorio, R. Sessoli, D. Mailly, and C. Paulsen, Phys. Rev. Lett. 82, 3903 (1999).

[10] L. D. Landau, Phys. Z. Sowjetunion 2, 46 (1932); C. Zener, Proc. R. Soc. London, Ser. A 137, 696 (1932); E. C. G. St"uckelberg, Helv. Phys. Acta 5, 369 (1932).

[11] Y. Kayanuma, J. Phys. Soc. Jpn. 53, 108 (1984).

[12] E. Keçecioğlu and A. Garg, Phys. Rev. B 76, 134405 (2007).

[13] W. Wernsdorfer, S. Bhaduri, A. Vinslava, and G. Christou, Phys. Rev. B 72, 214429 (2005).

[14] J. Villain, F. Hartmann-Boutron, R. Sessoli, and A. Rettori, Europhys. Lett. 27, 159 (1994).
Greek symbols – w-greek.sty

\begin{verbatim}
\alpha \beta \gamma \delta \epsilon \varepsilon \zeta \eta \\
\theta \vartheta \iota \kappa \lambda \mu \nu \xi \\
\omicron \omicron \tau \upsilon \varpi \phi \chi \\
\varphi \varrho \chi \psi \omega \\
\Gamma \Lambda \Sigma \Psi \\
\Delta \Xi \Upsilon \Omega \\
\Theta \Pi \Phi
\end{verbatim}

Table 1: Slanted greek letters

\begin{verbatim}
\Upalpha \Upbeta \Upsilon \vartheta \upiota \upsilon \\
\Upvartheta \upvarpi \upvarpi \phi \upsigma \psi \\
\upsigma \upsigma \upsigma \upsigma \upsigma \upsigma \\
\Gamma \Lambda \Sigma \Psi \\
\Delta \Xi \Upsilon \Omega \\
\Theta \Pi \Phi
\end{verbatim}

Table 2: Upright greek letters
Table 3: Boldface variants of slanted greek letters

| Slanted Greek | Boldface Greek |
|---------------|---------------|
| \( \alpha \)  | \( \pmb{\alpha} \) |
| \( \theta \)   | \( \pmb{\theta} \) |
| \( \omicron \) | \( \pmb{\omicron} \) |
| \( \tau \)     | \( \pmb{\tau} \) |
| \( \beta \)    | \( \pmb{\beta} \) |
| \( \vartheta \) | \( \pmb{\vartheta} \) |
| \( \omicron \) | \( \pmb{\omicron} \) |
| \( \upsilon \) | \( \pmb{\upsilon} \) |
| \( \gamma \)   | \( \pmb{\gamma} \) |
| \( \iota \)    | \( \pmb{\iota} \) |
| \( \varpi \)   | \( \pmb{\varpi} \) |
| \( \delta \)   | \( \pmb{\delta} \) |
| \( \kappa \)   | \( \pmb{\kappa} \) |
| \( \rho \)     | \( \pmb{\rho} \) |
| \( \phi \)     | \( \pmb{\phi} \) |
| \( \epsilon \) | \( \pmb{\epsilon} \) |
| \( \lambda \)  | \( \pmb{\lambda} \) |
| \( \varrho \)  | \( \pmb{\varrho} \) |
| \( \chi \)     | \( \pmb{\chi} \) |
| \( \zeta \)    | \( \pmb{\zeta} \) |
| \( \nu \)      | \( \pmb{\nu} \) |
| \( \varsigma \) | \( \pmb{\varsigma} \) |
| \( \omega \)   | \( \pmb{\omega} \) |

Table 4: Boldface variants of upright greek letters

| Upright Greek | Boldface Greek |
|---------------|---------------|
| \( \alpha \)  | \( \pmb{\alpha} \) |
| \( \theta \)   | \( \pmb{\theta} \) |
| \( \omicron \) | \( \pmb{\omicron} \) |
| \( \tau \)     | \( \pmb{\tau} \) |
| \( \beta \)    | \( \pmb{\beta} \) |
| \( \vartheta \) | \( \pmb{\vartheta} \) |
| \( \omicron \) | \( \pmb{\omicron} \) |
| \( \upsilon \) | \( \pmb{\upsilon} \) |
| \( \gamma \)   | \( \pmb{\gamma} \) |
| \( \iota \)    | \( \pmb{\iota} \) |
| \( \varpi \)   | \( \pmb{\varpi} \) |
| \( \delta \)   | \( \pmb{\delta} \) |
| \( \kappa \)   | \( \pmb{\kappa} \) |
| \( \rho \)     | \( \pmb{\rho} \) |
| \( \phi \)     | \( \pmb{\phi} \) |
| \( \epsilon \) | \( \pmb{\epsilon} \) |
| \( \lambda \)  | \( \pmb{\lambda} \) |
| \( \varrho \)  | \( \pmb{\varrho} \) |
| \( \chi \)     | \( \pmb{\chi} \) |
| \( \zeta \)    | \( \pmb{\zeta} \) |
| \( \nu \)      | \( \pmb{\nu} \) |
| \( \varsigma \) | \( \pmb{\varsigma} \) |
| \( \omega \)   | \( \pmb{\omega} \) |

| Upright Greek | Boldface Greek |
|---------------|---------------|
| \( \Gamma \) | \( \pmb{\Gamma} \) |
| \( \Delta \) | \( \pmb{\Delta} \) |
| \( \Theta \) | \( \pmb{\Theta} \) |
| \( \Sigma \) | \( \pmb{\Sigma} \) |
| \( \Psi \)   | \( \pmb{\Psi} \) |
| \( \Omega \) | \( \pmb{\Omega} \) |
| \( \Upsilon \)| \( \pmb{\Upsilon} \) |