Stochastic Landau-Zener model, and experimental estimates of dephasing time in molecular magnets.

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Quantum tunneling of the magnetization in magnetic molecules (MM) with high spin value is a fascinating subject which contrasts clean and accurate experimental data with sophisticated theoretical models. At the heart of these models stands the Landau [1] and Zener [2] (LZ) derivation of quantum tunneling between levels, which at resonance have a tunnel splitting Δ, but are brought in to and out off resonance by a time-dependent field. This theory predicts transition probabilities, however, it has not been able to account for the size of the magnetization jumps in molecular magnets. In fact, the discrepancy between Δ deduced from LZ experiments [3] and the one calculated from spectroscopic data is more than three orders of magnitudes [4]. In these circumstances it might be essential to analyze experiments using a broader LZ theory which includes stochastic fluctuations produced by the environment. Such a theory was developed by Shimshoni and Stern (SS) [5]. The SS theory takes into account the dephasing effect due to stochastic field fluctuations. Combining this theory with measurements of dephasing times for MM could lead to a revision in tunnel splitting calculations. But, as far as we know, there are no estimates for dephasing time of MM. The purpose of the present work is to highlight the importance of dephasing in tunneling experiments and to measure the dephasing time.

First we revisit the SS theory, limiting the discussion to the parameter range relevant to MM. This will be done in a tutorial manner in the hope that even a non experienced reader will be able to follow the calculations. In order to produce a formula we assume, as did SS, a weak-coupling between the spins and the environment, in a sense that will be defined below. We show how ignoring dephasing time can lead to erroneous estimates of Δ. Second we review muon spin relaxation experiment on isotropic ($\Delta = 0$) MM with varying spin values. These experiments provide information on the source of dephasing and an estimate of dephasing times. In light of our finding we recognize that weak-coupling is not the correct assumption for MM. Therefore, we set the stage for further theoretical developments.

1 Landau-Zener model in the presence of stochastic field fluctuations

We use the simplest Hamiltonian appropriate for the Landau-Zener problem. It is the Hamiltonian of a spin 1/2 which has a resonance tunnel splitting Δ at $t = 0$, and a time-dependent magnetic field αt in the z direction. The Hamiltonian is given by

$$\mathcal{H}_0 = \alpha t S_z + \Delta S_x \tag{1}$$

where $S_z = \sigma_z/2$, $S_x = \sigma_x/2$, and the σs are the Pauli matrixes. The Schrödinger equation could be written in a dimensionless form as

$$i\frac{t_T}{t_Z}\frac{\partial}{\partial y}\left|n\right\rangle = (yS_z + S_x)\left|n\right\rangle \tag{2}$$

where

$$t_z = \Delta/\alpha \tag{3}$$

is the Zener time [2],

$$t_T = \hbar/\Delta \tag{4}$$

is the tunneling time and

$$y = t/t_z \tag{5}$$

is dimensionless time.

Let us define the states $|+\rangle = [1, 0]$ and $|-\rangle = [0, 1]$. We are interested in the LZ probability that a spin prepared at time $t = -\infty$ in the low energy state $|+\rangle$ will be in the high energy state at $t = \infty$ which is again the $|+\rangle$ state. For this purpose we have to calculate the matrix element C_{LZ}

$$C_{LZ} = \langle +| U |+\rangle$$

where U is the time propagator operator. If the Hamiltonian had been time independent this operator would have been

$$\exp(-iH_0 t/\hbar). \tag{6}$$

But it does depend on time and a more complicated and approximated expression for U will be given soon. The probability of changing energy states is given by

$$P_{LZ} = \left|C_{LZ}\right|^2.$$

Sometimes a different definition for P_{LZ} is used where it is the probability of flipping energy states. In this case the spin stays in the low energy state throughout the field sweep. However, the two definitions sum up to 1 and extracting one from the other is trivial.

In the standard LZ model practically no transitions are taking place at very negative or very positive times. The transitions essentially take place within the Zener time scale t_z around $t = 0$. This is demonstrated in Fig. 1(a) which is a numerical solution of Eq. 2 taken from Ref. [6] as a function of time for three different values t_Z/t_T. Clearly most of the action is happening within t_z. The asymptotic case $t = \infty$ can be solved analytically [1, 2] and

$$P_{LZ} = \exp\left(-\frac{\pi\Delta^2}{2\hbar\alpha}\right) = \exp\left(-\frac{\pi t_Z}{2t_T}\right). \tag{7}$$

However, the solution involves reducing Eq. 2 to the Weber equation, which is not very well known in physics, and do not provide grate insight to the problem. We will take an approximation approach based on the SS theory.

The SS formulation of the problem gives a result similar to Eq. 7 and provides a natural platform for adding a fluctuating field. The solution starts by finding the instantaneous eigenstates and eigenvalues of the Hamiltonian in Eq. 1. These are

$$|\sigma_+(t)\rangle = \frac{\sqrt{2}}{2\sqrt{\Delta^2 + \alpha^2 t^2 + \alpha t\sqrt{\Delta^2 + \alpha^2 t^2}}}[\alpha t + \sqrt{\Delta^2 + \alpha^2 t^2}, \Delta] \tag{8}$$

with the eigenvalue

$$E_+ = +\frac{1}{2}\sqrt{\Delta^2 + \alpha^2 t^2} \tag{9}$$

and

$$|\sigma_-(t)\rangle = \frac{\Delta\sqrt{2}}{2\sqrt{\Delta^2 + \alpha^2 t^2 - \alpha t\sqrt{\Delta^2 + \alpha^2 t^2}}}[\alpha t - \sqrt{\Delta^2 + \alpha^2 t^2}, \Delta] \tag{10}$$

with the eigenvalue

$$E_- = -\frac{1}{2}\sqrt{\Delta^2 + \alpha^2 t^2}. \tag{11}$$

They are named according to their instantaneous energy. The two energy levels, normalized by Δ, are presented in Fig. 1(b) as a function of y (see Eq. 5) by the solid lines. We expect the instantaneous states and energies to be a useful concept in the adiabatic limit, namely, when the sweep rate is small. Looking at Eqs. 2 and 3 this means

$$\frac{t_T}{t_Z} < 1. \tag{12}$$

At $t \to -\infty$ we find that

$$|\sigma_-(-\infty)\rangle = |+\rangle$$

and at $t \to \infty$

$$|\sigma_+(\infty)\rangle = |+\rangle\,,$$

so that we need to calculate

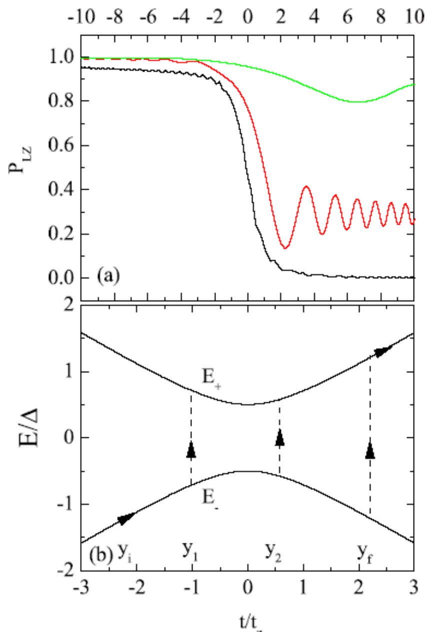

Fig. 1. (a) Landau-Zener transition probability as a function of normalized time reproduced from Ref. [6] for three values of t_Z/t_T: 0.05 (top), 0.4 (middle) and 5 (bottom). (b) Solid lines show the instantaneous energy levels as a function of normalized time in the Landau-Zener problem. Dashed lines are a schematic representation of the paths the spin can take when tunneling from the low energy state to the high energy state at times $t_j = y_j t_Z$. The transition amplitude is a sum of all paths with the appropriate matrix element as given by Eq. 16.

$$C_{LZ} = \langle \sigma_+(\infty) | \, U \, | \sigma_-(-\infty) \rangle \, .$$

To actually perform this calculation we divide the time into small segments and assume that we are allowed to use Eq. 6 (with $\hbar = 1$) in each segment, so that

$$U = \prod_{j=1}^{\infty} e^{-iH_0(t_j)\delta t} . \tag{13}$$

We also define the identity operator for each point in time

$$I_j = |\sigma_+(t_j)\rangle \langle \sigma_+(t_j)| + |\sigma_-(t_j)\rangle \langle \sigma_-(t_j)| \, . \tag{14}$$

We are now in position to perform the calculation. We do it by inserting this identity between every two exponents in Eq. 13. For example, let's divide the time between the initial time t_i and the final time $t_f = t_i + 2\delta t$ into two segment by introducing t_1 in between. In this case

$$C_{LZ} = \langle\sigma_+(t_f)|\, e^{-iH_0(t_1)\delta t}\, |\sigma_-(t_i)\rangle \tag{15}$$

and inserting Eq. 14 gives

$$C_{LZ} = \langle\sigma_+(t_f)|\, [|\sigma_+(t_1)\rangle\, \langle\sigma_+(t_1)| + |\sigma_-(t_1)\rangle\, \langle\sigma_-(t_1)|]\, e^{-iH_0(t_1)\delta t}\, |\sigma_-(t_i)\rangle\, .$$

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$$C_{LZ} = \langle\sigma_+(t_f)|\sigma_+(t_1)\rangle\, \langle\sigma_+(t_1)|\sigma_-(t_i)\rangle\, e^{-iE_+(t_1)\delta t}$$
$$+ \langle\sigma_+(t_f)|\sigma_-(t_1)\rangle\, \langle\sigma_-(t_1)|\sigma_-(t_i)\rangle\, e^{-iE_-(t_1)\delta t}.$$

We evaluate the bracket products to the lowest order in δt. For this purpose we approximate $|\sigma_-(t_1)\rangle$ using the time derivative

$$\left|\sigma'_-\right\rangle = \frac{d}{dt}\, |\sigma_-(t)\rangle$$

at the later time segment so that

$$\langle\sigma_+(t_f)|\sigma_-(t_1)\rangle \approx -\left\langle\sigma_+(t_f)|\sigma'_-(t_f)\right\rangle \delta t$$

and

$$\langle\sigma_+(t_1)|\sigma_-(t_i)\rangle \approx -\left\langle\sigma_+(t_1)|\sigma'_-(t_1)\right\rangle \delta t$$

since $\langle\sigma_+(t)|\sigma_-(t)\rangle = 0$. Similarly, to the lowest order in δt

$$\langle\sigma_-(t_1)|\sigma_-(t_i)\rangle = \langle\sigma_+(t_f)|\sigma_+(t_1)\rangle \approx 1.$$

Using these approximations in Eq. 15 gives

$$C_{LZ} = -\left\langle\sigma_+(t_f)|\sigma'_-(t_f)\right\rangle \delta t e^{-iE_-(t_1)\delta t} - \left\langle\sigma_+(t_1)|\sigma'_-(t_1)\right\rangle \delta t e^{-iE_+(t_1)\delta t}.$$

Now let's repeat the same exercise by dividing the time into three segments and introducing t_1 and t_2 in between t_i and t_f so that

$$C_{LZ} = \langle\sigma_+(t_f)|\, e^{-iH_0(t_2)\delta t} e^{-iH_0(t_1)\delta t}\, |\sigma_-(t_i)\rangle\, .$$

Again, inserting Eq. 14 behind the exponents gives

$$C_{LZ} = \langle\sigma_+(t_f)|\, [|\sigma_+(t_2)\rangle\, \langle\sigma_+(t_2)| + |\sigma_-(t_2)\rangle\, \langle\sigma_-(t_2)|]\, e^{-iH_0(t_2)\delta t}$$
$$\times [|\sigma_+(t_1)\rangle\, \langle\sigma_+(t_1)| + |\sigma_-(t_1)\rangle\, \langle\sigma_-(t_1)|]\, e^{-iH_0(t_1)\delta t}\, |\sigma_-(t_i)\rangle\, .$$

We look for cases where there is only one transition, since every transition introduces a factor δt. We also apply the Hamiltonians backwards and get

$$C_{LZ} = \langle\sigma_+(t_f)|\sigma_+(t_2)\rangle\, \langle\sigma_+(t_2)|\sigma_+(t_1)\rangle\, \langle\sigma_+(t_1)|\sigma_-(t_i)\rangle\, e^{-iE_+(t_2)\delta t} e^{-iE_+(t_1)\delta t}$$
$$+ \langle\sigma_+(t_f)|\sigma_+(t_2)\rangle\, \langle\sigma_+(t_2)|\sigma_-(t_1)\rangle\, \langle\sigma_-(t_1)|\sigma_-(t_i)\rangle\, e^{-iE_+(t_2)\delta t} e^{-iE_-(t_1)\delta t}$$

$$+\langle\sigma_+(t_f)|\sigma_-(t_2)\rangle\langle\sigma_-(t_2)|\sigma_-(t_1)\rangle\langle\sigma_-(t_1)|\sigma_-(t_i)\rangle e^{-iE_-(t_2)\delta t}e^{-iE_-(t_1)\delta t}$$

Using the same rules as before we find

$$\begin{aligned} C_{LZ} = &-\left\langle\sigma_+(t_1)|\sigma'_-(t_1)\right\rangle\delta t e^{-iE_+(t_2)\delta t}e^{-iE_+(t_1)\delta t} \\ &-\left\langle\sigma_+(t_2)|\sigma'_-(t_2)\right\rangle\delta t e^{-iE_+(t_2)\delta t}e^{-iE_-(t_1)\delta t} \\ &-\left\langle\sigma_+(t_f)|\sigma'_-(t_f)\right\rangle\delta t e^{-iE_-(t_2)\delta t}e^{-iE_-(t_1)\delta t}. \end{aligned}$$

This expression has a graphical representation depicted in Fig. 1(b). Transitions are occurring at some time t. We take the exponent of $-i\delta t$ times the sum of the low energies at the t_js $[E_-(t_j)]$ until the transition. From the transition onward we do the same thing using the high energy $[E_+(t_j)]$ until the final time t_f. The exponential factor per transition is multiplied by $\left\langle\sigma_+(t)|\sigma'_-(t)\right\rangle$ at the time of the transition. Finally, we sum all contributions.

If we divide the time into an infinite number of segments and substitute $t_i \to -\infty$ and $t_f \to \infty$, we will find that

$$C_{LZ} = -\int_{-\infty}^{\infty} dt' \left\langle\sigma_+(t')|\sigma'_-(t')\right\rangle e^{-i\int_{t'}^{\infty}E_+(\tau)d\tau - i\int_{-\infty}^{t'}E_-(\tau)d\tau} \tag{16}$$

where t' now represents the time at which a transition is taking place. Next using Eqs. 9 and 11 we replace $E_-(\tau)$ by $-E_+(\tau)$. To this we add zero in the form of

$$i\int_{-\infty}^{t'}E_+(\tau)d\tau + i\int_{t'}^{\infty}E_+(\tau)d\tau - i\int_{-\infty}^{\infty}E_+(\tau)d\tau$$

which leads to

$$-i\int_{t'}^{\infty}E_+(\tau)d\tau - i\int_{-\infty}^{t'}E_-(\tau)d\tau = 2i\int_{-\infty}^{t'}E_+(\tau)d\tau - i\int_{-\infty}^{\infty}E_+(\tau)d\tau.$$

We give the following name

$$A(t') = \left\langle\sigma_+(t')|\sigma'_-(t')\right\rangle$$

and find using Eqs. 10 and 8 that

$$A(t') = \frac{\Delta\alpha}{2(\Delta^2 + (\alpha t')^2)}. \tag{17}$$

Similarly we name

$$\phi(t') = 2\int_{-\infty}^{t'}E_+(\tau)d\tau = \int_{-\infty}^{t'}\sqrt{\Delta^2 + (\alpha\tau)^2}d\tau. \tag{18}$$

Thus

$$C_{LZ} = -e^{-i\phi(\infty)/2} \int_{-\infty}^{\infty} dt' A(t') e^{i\phi(t')}. \tag{19}$$

In the adiabatic limit (Eq. 12) this integral can be solved using a saddle point approximation [7] as we demonstrate now. Since we are going to take the absolute value of C_{LZ} we can ignore all multiplying phases and express the integral in dimensionless form

$$D_{LZ} = \frac{1}{2} \int_{-\infty}^{\infty} dy \frac{1}{1+y^2} e^{i \frac{t_Z}{t_T} w(y)} \tag{20}$$

where

$$w(y) = \int_0^y \sqrt{1+x^2} dx.$$

There are no poles between the real axis and an axis running parallel to it through, but avoiding from below, the point i. We therefore perform the integral along this new axis. We need to find y_c where $w(y)$ is stationary by taking

$$w' \equiv \frac{dw(y)}{dy} = \sqrt{1+y^2} = 0 \tag{21}$$

which gives $y_c = \pm i$. We expand $w(y)$ around y_c using small values of x so that

$$w(y) = w_c + \int_0^{y-y_c} \sqrt{1+(x+y_c)^2} dx \simeq w_c + \sqrt{2y_c} \frac{2}{3} (y-y_c)^{3/2} \tag{22}$$

where

$$w_c = \int_0^{y_c} \sqrt{1+x^2} dx = \pm i\pi/4.$$

The integral of Eq. 20 is done by changing variables $dw = w'dy$ and using Eq. 21

$$D_{LZ} = \frac{1}{2} \int_{-\infty}^{\infty} \frac{dw}{w'(1+y^2)} e^{i \frac{t_Z}{t_T} w} = \frac{1}{2} \int_{-\infty}^{\infty} \frac{dw}{(w')^3} e^{i \frac{t_Z}{t_T} w}.$$

From Eqs. 22 and 21

$$(w')^3 = (2y_c)^{3/2} (y-y_c)^{3/2} = 3y_c (w-w_c)$$

so that finally, by closing the path of integration in the upper part of the complex plane, we get

$$D_{LZ} = \frac{1}{6y_c} \int_{-\infty}^{\infty} \frac{dw}{(w-w_c)} e^{i \frac{t_Z}{t_T} \phi} = \frac{\pi i}{3y_c} e^{-\frac{\pi t_Z}{4 t_T}}$$

yielding

$$P_{LZ} = \left(\frac{\pi}{3}\right)^2 \exp\left(-\frac{\pi \Delta^2}{2\hbar\alpha}\right).$$

This is only slightly different from the exact result in Eq. 7.

The calculation using the SS formalism clearly shows that P_{LZ} is a consequence of interference of different paths. If instead of summing transition amplitude we would sum transition probabilities $|A(t')|^2$ using discretization of time based on the uncertainty principle $\hbar/|2E_+(t')|$ we would find

$$\frac{1}{4}\int_{-\infty}^{\infty} |A(t')|^2 \frac{\hbar}{2E_+(t')} dt' = \frac{35\pi\hbar\alpha}{1024\Delta^2}$$

which is very different from P_{LZ}.

Now let's introduce dephasing. The starting point is the LZ transition probability obtained by taking the absolute value of Eq. 19

$$P_{LZ} = |C_{LZ}|^2 = \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 A(t_1)A(t_2)e^{i[\phi(t_1)-\phi(t_2)]}.$$

We consider the simplest case where a fluctuating field fluctuates in the z direction, namely, the Hamiltonian is

$$\mathcal{H} = [\alpha t + 2B(t)]S_z + \Delta S_x$$

where $B(t)$ is a stochastic field. We include μ_B in the definition of B. This is equivalent to introducing noise to the sweep rate α which will affect both $A(t')$ and $\phi(t')$. The effect on $A(t')$ involves energy non-conserving transitions between states, which is equivalent to T_1 processes. The effect on $\phi(t')$ involves dephasing similar to T_2. Usually T_2 is shorter than T_1 so we will concentrate on the stronger effect. In other words we ignore the effect of B on the $A(t')$ and simply consider its impact on the phases. We now have to average P_{LZ} over different realizations of the noise $B(t)$. We rename this stochastic LZ transition probability as SS probability and write

$$\langle P_{SS}\rangle = \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 A(t_1)A(t_2)\left\langle e^{i[\phi(t_1)-\phi(t_2)]}\right\rangle. \tag{23}$$

As a result of the fluctuations in B the phase ϕ will have an average part $\langle\phi(t)\rangle$ which is not random and given by Eq. 18, and a part $\delta\phi$ which is different for different realizations of B, therefore,

$$\left\langle e^{i[\phi(t_1)+\delta\phi(t_1)-\phi(t_2)-\delta\phi(t_2)]}\right\rangle = e^{i[\langle\phi(t_1)\rangle-\langle\phi(t_2)\rangle]}\left\langle e^{i[\delta\phi(t_1)-\delta\phi(t_2)]}\right\rangle.$$

We assume that $\langle\exp(i[\delta\phi(t_1)-\delta\phi(t_2)])\rangle$ is a function of $t_1 - t_2$ and introduce a phenomenological dephasing time τ_ϕ which is defined as

$$\left\langle e^{i[\delta\phi(t_1)-\delta\phi(t_2)]}\right\rangle \simeq e^{-|t_1-t_2|/\tau_\phi}. \tag{24}$$

SS related τ_ϕ to the dynamic properties of $B(t)$. We will not give this derivation here and simply mention that if

$$\langle B(t)B(0)\rangle = B^2\exp(-\nu t) \tag{25}$$

then

$$\frac{1}{\tau_\phi} = \frac{B^2}{\hbar^2\nu}. \tag{26}$$

For the dynamic fluctuations to be interesting the field must fluctuate several times before the tunneling process is over, therefore the interesting case is the fast fluctuation limit

$$\nu t_Z > 1. \tag{27}$$

The important point to carry to the next section is that the environment alone determines the dephasing time. If we can determine the dephasing time for one kind of molecule in a given environment, and if we believe the environment does not change between different molecules, then we know the dephasing time for other molecules.

Inserting Eqs. 17, 18 and 24 into 23 we find

$$\langle P_{SS}\rangle = \frac{1}{4}\int_{-\infty}^{\infty} du \int_{-\infty}^{\infty} ds \frac{1}{1+u^2}\frac{1}{1+s^2}\exp\left(i\frac{t_Z}{t_T}\int_s^u \sqrt{1+v^2}dv\right)\exp\left(-\frac{|u-s|}{u_\phi}\right) \tag{28}$$

where

$$u_\phi = \tau_\phi/t_Z.$$

Evaluation of this integral is not simple. To date SS have done this analytically for weak dephasing only where the dephasing time τ_ϕ is long compared to the resonance tunneling time t_T given in Eq. 4. In this case we have

$$\frac{t_T}{\tau_\phi} = \frac{B^2}{\Delta\hbar\nu} < 1. \tag{29}$$

Since this case means that B is small, it is named the weak-coupling limit. Another requirement for analytic evaluation of the integral is that the dephasing is taking place within the Zener time, namely, $\tau_\phi/t_Z < 1$. One can call this requirement long LZ time, and it is expressed as

$$\frac{\tau_\phi}{t_Z} = \frac{\hbar^2\nu\alpha}{B^2\Delta} < 1. \tag{30}$$

Put in other words, analytical evaluation of Eq. 28 is provided only for the time scales order

$$t_Z > \tau_\phi > t_T. \tag{31}$$

In the adiabatic (Eq. 12), fast fluctuation (Eq. 27), weak coupling (Eq. 29), and long LZ time (Eq. 30) limits, the integral in Eq. 28 can be evaluated [5]; the answer is

$$\langle P_{SS}\rangle \simeq \frac{\tau_\phi \alpha}{\Delta}\left(e^{\frac{2\Delta}{\alpha\tau_\phi}} P_{LZ} + \left\{ \frac{\hbar}{\Delta\tau_\phi} \right\}^2 \right). \tag{32}$$

It is clear from this expression that for a proper evaluation of Δ from a tunneling experiment τ_ϕ must be determined. If one insists on fitting experimental data with a LZ type expression, as in Eq. 7, using an observed tunnel splitting Δ_{obs} one finds, in terms of the three time scales, that

$$\frac{\Delta_{obs}^2}{\Delta^2} = -\frac{2t_T}{\pi t_Z} \ln \frac{\tau_\phi}{t_Z}\left(e^{\frac{2t_z}{\tau_\phi}} P_{LZ} + \left\{ \frac{t_T}{\tau_\phi} \right\}^2 \right).$$

Interestingly, due to the dephasing, the observed tunnel splitting becomes sweep rate dependent.

When considering experimental difficulties, the four limits leave a very narrow range of parameters in which Eq. 32 is valid. For example, for $\Delta = 10^{-7}$ K, $\alpha/\mu_B = 10^{-4}$ T/s, $B/\mu_B = 0.1$ G, and $\nu = 5\times 10^8$ sec^{-1} we find that $t_z = 1.5\times 10^{-3}$ sec, $\tau_\phi = 6.4\times 10^{-4}$ sec, and $t_T = 7.6\times 10^{-5}$ sec, so that the order of time scales given in Eq. 31 holds, and $\nu t_Z > 1$. In this case $\Delta_{obs} = 0.4\times 10^{-7}$ K which is smaller than Δ. Thus, dephasing increases the probability of moving from the low energy state to the higher one, or, decreases the probability of staying in the low energy state.

2 Experimental dephasing time estimates

We extract the dephasing time in real material using muons coupled to the electronic spins of isotropic MM that experience only the stochastic field. The leading terms for such an Hamiltonian are

$$\mathcal{H} = -2\mu_B \left[\mathbf{H} + \mathbf{B}(t)\right]\mathbf{S} + \hbar^{\mu}\gamma \left[\mathbf{H} + \mathbf{SA}\right]\mathbf{I}$$

where $\mathbf{S}$ is the electronic spin, $\mathbf{I}$ is the muon spin, $\mathbf{H}$ is the external field, $\mathbf{B}$ is the stochastic field, $\gamma_\mu = 85.162$ MHz/kG is the muon gyromagnetic ratio, μ_B is the Bohr magneton, and $\mathbf{A}$ is a coupling matrix. In this section we use a definition of $\mathbf{B}$ which does not include μ_B since the electronic spin and the muon spins have different gyromagnetic ratios. We ignore a term of the form $\mathbf{B}(t)\mathbf{I}$ since the field experienced by the muon from the molecular spins is greater than this term. Due to the fluctuating field $\mathbf{B}$, $\mathbf{S}$ will vary in time. The simplest assumption that one can make is that the correlation function $\langle\{\mathbf{S}(t),\mathbf{S}(0)\}\rangle$, where $\{\}$ stands for anticomutator, decay exponentially. The decay rate is determined by the dynamic properties of $\mathbf{B}(t)$ which is produced by the environment of the molecules. Therefore we expect

$$\{\mathbf{S}(t), \mathbf{S}(0)\} = 2S^2 \exp(-t/\tau_\phi). \tag{33}$$

A priori it is possible that τ_ϕ will be H-dependent but we will show experimentally that this is not the case for $H < 2$ kG.

The muon, which is prepared with 100% polarization, will decay towards its equilibrium polarization with a decay rate

$$\frac{1}{^\mu T_1} = \frac{2A^2\tau_\phi}{1 + (^\mu\gamma H \tau_\phi)^2} \tag{34}$$

where we assumed for simplicity that $\mathbf{A}$ is diagonal and isotropic as well. By measuring $^\mu T_1$ as a function of H^2 and fitting the measurement to

$$^\mu T_1 = m + nH^2 \tag{35}$$

one can obtain τ_ϕ from

$$\tau_\phi = \left(\frac{n}{m^\mu\gamma^2}\right)^{1/2}. \tag{36}$$

Salman *et al.* [8] performed such an experiment for three different isotropic MM with different spin value. In these systems no tunneling is observed due to the absence of a tunnel splitting Δ. However, spin dynamics is observed even at very low temperatures ($T = 50$ mK) with no temperature dependence over a wide temperature range [9].

The molecules were $[Cr\{(CN)Cu(tren)\}_6\,](ClO_4)_{21}$, $[Cr\{(CN)Ni(tetren)\}_6\,](ClO_4)_9$ [10, 11] and $[Cr\{(CN)Mn(tetren)\}_6](ClO_4)_9$ [12], which are labeled as $CrCu_6$, $CrNi_6$ and $CrMn_6$, respectively. In these molecules a Cr(III) ion is surrounded by six cyanide ions, each bonded to a Cu(II), Ni(II) or Mn(II) ion. Their magnetic moments of $CrCu_6$, $CrNi_6$ and $CrMn_6$ is $\frac{9}{2}\, g\mu_B$, $\frac{15}{2}\, g\mu_B$ and $\frac{27}{2}\, g\mu_B$, respectively. High field ESR measurements (on $CrNi_6$) [5] and susceptibility measurements (on $CrCu_6$, $CrNi_6$ and $CrMn_6$) found no evidence for anisotropy. This is consistent with the octahedral character of the molecules.

In Fig. 2 we reproduce the data from Ref. [8] where the relaxation time $T_1^\mu(H)$ is plotted at $T \to 0$ as a function of H^2 for all compounds, and for fields up to 2 kG (note the axis break). T_1^μ obeys Eq. 35 in this range. This is consistent with the assumption that for low H the field experience by the muon, which stems from the molecules, and hence the molecular spin autocorrelation function, can be described by a single correlation time τ_ϕ, and that τ_ϕ is field-independent.

From the linear fits in Fig. 2, and using Eq. 36, it was found that $\tau_\phi = 7 \pm 1$ nsec for $CrCu_6$, $\tau_\phi = 10 \pm 1$ nsec for $CrNi_6$ and $\tau_\phi = 11 \pm 1$ nsec for $CrMn_6$. According to Eq. 26 this kind of dephasing time could be generated by a field $B \sim 1$ G fluctuating with a fluctuation rate of $\nu \sim 10^6$ sec^{-1}.

3 Conclusions

It is highly significant that τ_ϕ is nearly spin-independent. Since τ_ϕ is determined by the environment in which the molecules are embedded, its S-

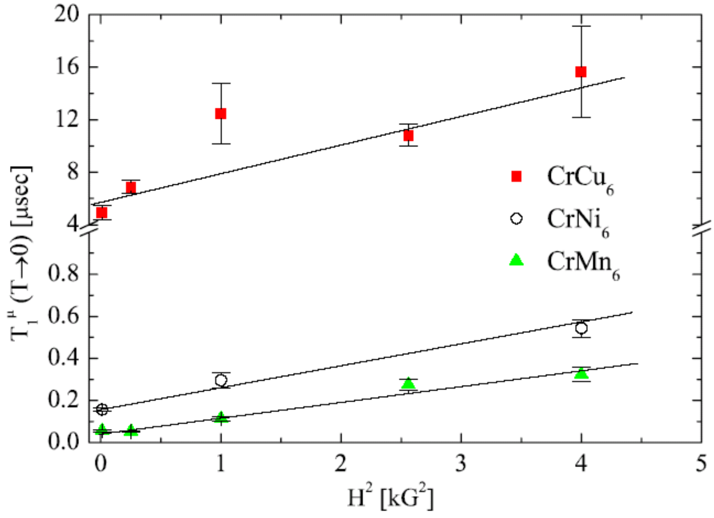

Fig. 2. The relaxation time at $T \sim 100$ mK as a function of H^2 for $CrCu_6$, $CrNi_6$ and $CrMn_6$ with sping value $S = 9/2$, $15/2$, $27/2$. The solid lines are linear fits. Data are reproduced from Ref. [8]

independence means that coupling to other molecules or to phonons is not responsible for τ_ϕ. This can be understood by examining the Bloch equation which govern the spin motion. In zero external field this equation is given by

$$\frac{d\widehat{\mathbf{S}}}{dt} = {}^{e}\gamma[\widehat{\mathbf{S}} \times \mathbf{B}(t)]$$

where $\widehat{\mathbf{S}}$ is a unit vector in the direction of the magnetic moment. Only if $\mathbf{B}$ does not stem from other molecules or from spin-phonon coupling could the time scale for spin motion be S-independent, as found experimentally. We therefore conclude that at $T \to 0$ the stochastic field $\mathbf{B}(t)$ responsible for the MM spin motion most likely emanates from nuclear moments.

More importantly τ_ϕ is on the order of 10 nsec. As we argue before, we assume that this dephasing time is typical to high spin magnetic molecules made of transition metal ions embedded in a sea of other ions, including a large number of protons. Indeed, the three isotropic molecules reported here are different but have the same τ_ϕ. We have no reason to believe that τ_ϕ will be substantially different in Fe_8 for example. In Fe_8, the only molecule where as far as we know Δ_{obs} was measured, it was found to be on the order of 10^{-7} K and sweep rate dependent [3]. If this Δ_{obs} had been simply the intrinsic tunnel splitting Δ, then the tunneling time would have been $\hbar/\Delta \sim 7 \times 10^{-5}$ sec. This tunneling time is longer than the dephasing time $\tau_\phi = 10^{-8}$ sec. More over if, for example, $\alpha = 0.001$ T/sec, then the Zener time (for the 10 to -10 transition) $t_z = \Delta/(20\alpha) = 7 \times 10^{-5}$ sec. This makes the order of time scales $t_Z \sim t_T > \tau_\phi$. This order is very different from Eq. 31, and neither the LZ theory nor the SS theory are valid. However, it is conceivable that Δ_{obs} is not the intrinsic Δ, and that $\Delta > \Delta_{obs}$. If this is correct we might still be in the adiabatic limit and Δ_{obs} could be sweep rate dependent as was observed experimentally. However, to be in the $\tau_\phi > t_T$ range, it must be that $\Delta \gg \Delta_{obs}$ and in fact $\Delta > 10^{-3}$ K. It is more likely that in the MM the order of time scales is $t_Z > t_T > \tau_\phi$. For this case there is no theory available and a new approach is required.

4 Acknowledgments

The author is grateful for enlightening discussions with E. Shimshoni. The work is funded in part by the Russell Berrie Nanotechnology Institute.

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