P H Y S I C A L   R E V I E W   L E T T E R S

Experimental Estimates of Dephasing Time in Molecular Magnets

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Muon spin relaxation measurements in isotropic molecular magnets (MM) with a spin value S ranging from 7/2 to 27/2 are used to determine the magnitude and origin of dephasing time τ_ϕ of molecular magnets. It is found that $\tau_\phi \sim 10$ nsec with no S or ligand dependence. This indicates a nuclear origin for the stochastic field. Since τ_ϕ is a property of the environment, we argue that it is a number common to similar types of MM. Therefore, τ_ϕ is shorter than the Zener and tunneling times of anisotropic MM such as Fe_8 or Mn_4 for standard laboratory sweep rates. Our findings call for a stochastic Landau-Zener theory in this particular case.

Quantum tunneling of the magnetization in anisotropic molecular magnets (MM) with high spin value is a fascinating subject which contrasts clean and accurate experimental data with sophisticated theoretical models [1]. At the heart of these models stands the Landau [2] and Zener [3] (LZ) derivation of quantum tunneling between levels, which at resonance have a tunnel splitting Δ, but are brought into and out off resonance by a time-dependent field. This model can be described by the Hamiltonian $\mathcal{H}_0 = \beta t S_z + \Delta S_x$, where **S** is the electronic spin operator and β is proportional to the external field sweep rate dH/dt. The LZ theory predicts the transition amplitude C_{LZ} 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 $|+\rangle$, namely, $C_{LZ} = \langle +|U|+\rangle$ where U is the time propagator operator. The calculation of this amplitude has a path integral representation as demonstrated graphically in the inset of Fig. 1 [4–6]. In this inset, the solid lines show the instantaneous energies $E_\pm = \pm\frac{1}{2}\sqrt{\Delta^2 + \beta^2 t^2}$, and a single path is associated with a transition from the lower energy state to the upper energy state, which occurs at a specific time t'.

However, there is consensus among researchers that the tunneling in MM is incoherent due to interactions of the spin with a stochastic field **B**(t) which is produced by nuclear moments [6–10], and that the dephasing time of the quantum states must be taken into account. The dephasing time τ_ϕ is defined using the correlator of the stochastic field

$$\langle \mathbf{B}(t)\mathbf{B}(0)\rangle = \langle B^2\rangle \exp(-t/\tau_c), \tag{1}$$

as

$$\frac{1}{\tau_\phi} = \frac{\langle B^2\rangle \tau_c}{\hbar^2}. \tag{2}$$

When the dephasing time is very long, the transition probability P_{LZ} is given by the absolute value square, of the sum of the transition amplitudes, for different paths. This yields the famous expression

$$P_{LZ} = 1 - \exp\left(-\frac{\pi\Delta^2}{2\hbar\beta}\right) \tag{3}$$

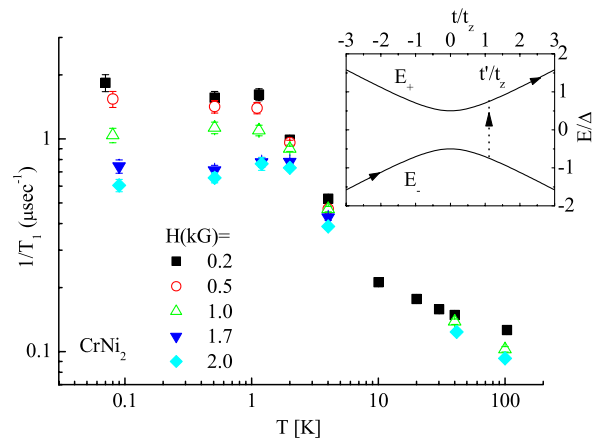of flipping states [11]. In contrast, if the dephasing time is

FIG. 1 (color online). The muon spin lattice relaxation rate $1/T_1$ as a function of temperature and field in the $CrNi_2$ ($S = 7/2$) high spin molecular magnet. Inset: the solid lines show the instantaneous energy levels as a function of time in the Landau-Zener problem. Dashed line is a schematic representation of a path the spin can take when tunneling from the low energy state to the high energy state at time t'/t_Z.

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very short, the interference between paths should be destroyed and transition probability should become a sum of instantaneous transition probabilities.

Therefore, there are four important time scales in the LZ problem: (I) the tunneling time $t_T = \hbar/\Delta$ which is set by the tunnel splitting, (II) the Zener time $t_z = \Delta/\beta$, which is the time segment around $t = 0$ where tunneling can occur during a field sweep in the adiabatic case ($t_T \ll t_z$), (III) the correlation time τ_c, and (IV) the dephasing time τ_ϕ over which different paths interfere coherently. Determining these time scales even roughly could help select the theory for the analysis of magnetization jump experiments. Moreover, theories are available only for particular orders of time scales, which might not be the realistic ones.

The theories addressing the stochastic LZ problem can be divided into two groups according to the type of stochastic field they use: Ising type with coupling $B_z(t)S_z$ or Heisenberg type with an $\mathbf{B}(t) \cdot \mathbf{S}$ term. In the Ising case Kayanuma [4] found modifications to the LZ formula for the order of time scales $\tau_c \ll \tau_\phi \ll (t_z t_T)^{1/2}$ and $\tau_c \ll \max[t_z, t_z t_T/\tau_\phi]$. In this case the transition probability is given by $P = [1 - \exp(-\pi t_z/t_T)]/2$. Therefore, when the transition is sudden ($t_T \gg t_z$) then $P = \pi \Delta^2/(2\hbar\beta)$ as in Eq. (3) at the same limit. Sinitsyn, Prokof'ev, and Bobrovitski [6] extended this work using macroscopic spin bath description of $B_z(t)$ and showed that Kayanuma's sudden result is correct if and only if $t_T \gg t_z$. In the Heisenberg case, Shimshoni and Stern found corrections to the LZ formula in all orders of time scales they examined. Here we mention just the interesting case of $\tau_c \ll \tau_\phi$ and $t_T \ll \tau_\phi \ll t_z$, where they found that $P \simeq 1 - (\tau_\phi/t_Z)[\exp(2t_Z/\tau_\phi)P_{LZ} + (t_T/\tau_\phi)^2]$ [5]. More theoretical work can be found in Ref. [12]. The consensus seems to be that when the field sweep is adiabatic $t_z \gg t_T$, the stochastic field modifies the LZ formula, and that in the sudden limit $t_T \gg t_z$ of the Ising case the dephasing time τ_ϕ has no impact on the tunneling probability. However, as far as we know there is no theory for the Heisenberg coupling when τ_ϕ is the shortest time scale in the problem.

Despite the importance of τ_ϕ determination in the LZ problem, today there is no experimental estimate of this time in the problem of magnetic quantum tunneling. The purpose of the present work is to provide such an estimate. We do so by measuring the dephasing times of isotropic molecular magnets ($\Delta = 0$) with different spin value and ligands, and we project the result to anisotropic MM such as Fe_8 or Mn_4. This allows us to set the order of t_z, t_T, and τ_ϕ. Our major finding is that τ_ϕ is the shortest time scale in the problem. Since nuclear dipolar coupling to the molecular spins involves all directions, we conclude that there is no relevant theory for the LZ problem in MM with stochastic field.

In addition to the contribution to the problem of magnetic quantum tunneling, our experiment has its own merit.

It is the first examination of magnetic fluctuation as a function of the spin value S. As such, it provides a new look at the interaction between spins and the lattice in the quantum (temperature independent) regime.

We determine the dephasing times of isotropic molecules by performing muon spin relaxation measurements on eight different MM with $\Delta \simeq 0$ and spin value ranging from $S = 7/2$ to $S = 27/2$. The major assumption here is that τ_ϕ is a property of the environment and not of the molecule [see Eq. (2)]. Therefore, if we determine τ_ϕ for one type of molecule, and if a different molecule has the same environment, it will have the same τ_ϕ. This assumption received experimental support recently in the work of Ardavan *et al.*. They showed using ESR that two different molecules, one with zero field splitting and the other without it, have the same electronic T_2 [13]. However, it also has advocates. Stamp, Tupitsyn, and Morello argue that the molecular electronic spin impacts the nuclear spin dynamic and therefore the dephasing time should depend on Δ so that $\tau_\phi \propto \Delta$ [8]. Encouraged by the experimental finding, we continue the presentation using our assumption.

What allows us to extract the dephasing time is the fact that our muons are coupled to the electronic spins of isotropic MM that experience only the stochastic and external fields. Therefore, the number of parameters needed to be determined in our experiment is minimal, and there is no need to know *a priori* the order of time scales. The leading terms for such a Hamiltonian are

$$\mathcal{H} = -2\mu_B[\mathbf{H} + \mathbf{B}(t)]\mathbf{S} + \hbar^\mu\gamma[\mathbf{H} + \mathbf{SA}]\mathbf{I}, \quad (4)$$

where $\mathbf{I}$ is the muon spin, $\mathbf{H}$ is the external field, $^\mu\gamma = 851.62$ MHz/T is the muon gyromagnetic ratio, μ_B is the Bohr magneton, and $\mathbf{A}$ is a coupling matrix. We ignore the $\mathbf{B}(t)\mathbf{I}$ term since the field experienced by the muon from the molecular spins is greater than this term. Because of 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 anticommutator, decays 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

$$\{\mathbf{S}(t), \mathbf{S}(0)\} = 2S^2\exp(-t/\tau_\phi) \quad (5)$$

with τ_ϕ set by Eq. (2). It is possible that τ_ϕ will be H dependent but we will show experimentally that this is not the case for $H \leq 2$ kG.

We investigated $CrCu_4$ ($S = 7/2$), $CrNi_2$ ($S = 7/2$), $CrNi_2Mn_4$ ($S = 13/2$), $CrNi_2Ni_4$ ($S = 15/2$), and $CrNiMn_5$ ($S = 20/2$). To this, we added data from a previous study of $CrCu_6$ ($S = 9/2$), $CrNi_6$ ($S = 15/2$), and $CrMn_6$ ($S = 27/2$) by Salman *et al.* [14]. These compounds, based on polycyanometalated precursors, are prepared following a step-by-step synthetic strategy. The key idea is to use polydentate amine ligands in order to avoid polymerization and get discrete entities with well-defined

spin and anisotropy [15,16]. Most of the compounds are fully described in the literature [17,18]. They may be divided into two groups: (i) isotropic high spin molecules ($CrCu_6$, $CrNi_6$, and $CrMn_6$) and (ii) nearly isotropic molecules with no detectable energy gap or small one ~1 K ($CrCu_4$, $CrNi_2$, $CrNiMn_5$, $CrNi_2Mn_4$, $CrNi_2Ni_4$).

In our μSR-T_1 experiments we measure the polarization $P(t, H)$ of a muon spin implanted in the sample, as a function of time t and magnetic field H, when the field is applied in the direction of the initial muon polarization. These experiments were performed at both ISIS and PSI, exploiting the long time window in the first facility for the slow relaxation of the low S molecules and the high time resolution in the second facility for the fast relaxation of the high S molecules. Typical raw μSR data are presented in Ref. [14]. The data for all samples are fitted to $P(H, t) = \exp(-\sqrt{t/T_1}) + Bg$, where Bg is a field and temperature independent background. This root exponential behavior is a consequence of the many different muon sites in the sample.

In Fig. 1 we depict the temperature dependence of $1/T_1$. As the temperature is lowered, the relaxation increases due to slowing down of the spin fluctuation as a result of the interactions between spins in the molecules. However, once the MM is formed, the spin dynamics is nearly temperature independent down to the milikelvin regime. All molecules show the same behavior. More raw T_1 data are presented in Ref. [14].

In Fig. 2 we depict T_1 as a function of H^2 for all the molecules measured to date. There is a large variation in the scale of T_1 between the different molecules. A linear dependence of the form $T_1 = m + nH^2$ is found in all cases, as demonstrated by the fitted solid line. This is in agreement with Ref. [14]. The difference between molecules is in the slope n and crossing of the line m. The dephasing time could be extracted from the standard theory of T_1 relaxation where

$$\frac{1}{T_1} = \frac{2A^2\tau_\phi}{1 + (^\mu\gamma H\tau_\phi)^2}. \qquad (6)$$

Although this expression is a result of perturbation expansion where **H** provides the quantization axis, it was demonstrated by numerical methods to be a good approximation even for $H \to 0$ [19]. Here we assumed for simplicity that **A** is diagonal and isotropic, but this assumption has no significance for our conclusions. τ_ϕ is obtained from

$$\tau_\phi = \left(\frac{n}{m^\mu\gamma^2}\right)^{1/2} \qquad (7)$$

for each molecule at the lowest temperature.

The main experimental finding of this work is presented in Fig. 3 where τ_ϕ^{-1} is plotted as a function of S for all the molecules. This plot shows that within experimental errors τ_ϕ is weakly dependent on the type of molecule used,
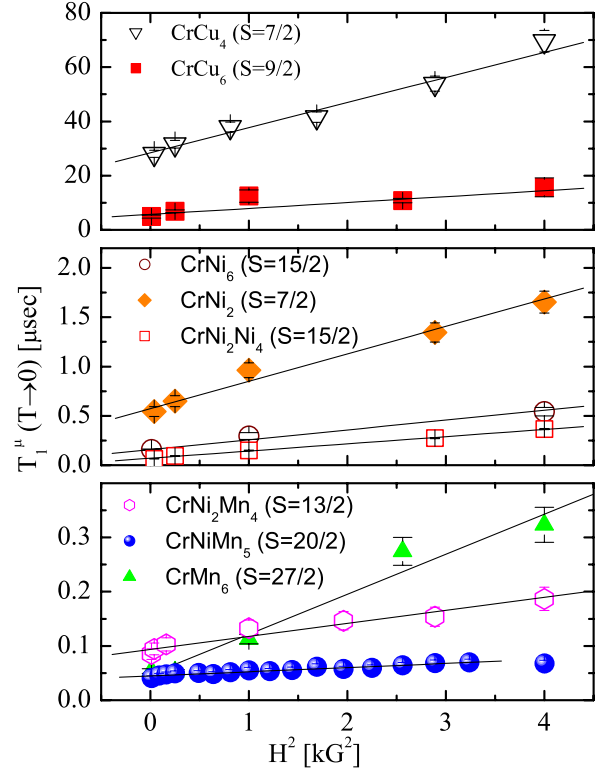

FIG. 2 (color online).   Muon T_1 at 100 mK vs field squared for all molecules including three from Ref. [14]. The solid lines are linear fits.

despite the large variations in T_1. In particular, τ_ϕ is weakly dependent on S or the ligand. To emphasize this conclusion we fit the data to three different power laws: $\tau_\phi^{-1} \propto$ constant, S, and S^2. The quality of the fit expressed as the value of the reduced χ^2 is shown on the graph. The $\tau_\phi^{-1} =$ const gives an order of magnitude better fit than the other power laws. It is also interesting to compare our finding of $\tau_\phi \sim 10$ nsec to other experiments. In the deu-
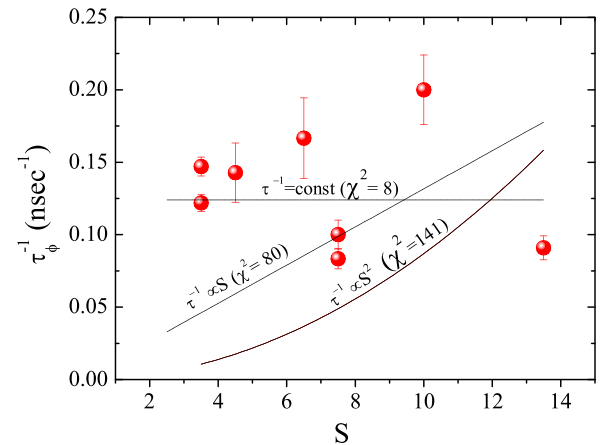

FIG. 3 (color online).   Dephasing rate τ_ϕ^{-1} extracted from the muon relaxation data as a function of spin value S of the various magnetic molecules. The solid lines are fits to power laws as indicated in the figure. χ represent the quality of the fit.

terated molecules Cr_7Mi and Cr_7Mn the ESR T_2 (interpreted here as τ_ϕ) is 3 μ sec [13]. Had the samples were not deuterated, τ_ϕ would have been 80 nsec due to the gyromagnetic ratio between protons and deuterium. In the V_{15} molecule, $\tau_\phi \sim 2$ nsec [20].

It is highly significant that τ_ϕ is nearly spin and ligand independent. Since τ_ϕ is determined by the environment in which the molecules are embedded, its S independence means that coupling to other molecules or to phonons is not responsible for τ_ϕ. In both these mechanisms the field **B** experienced by a given molecule depends on S, and according to Eq. (2) we would expect an S-dependent τ_ϕ. We therefore conclude that at $T \rightarrow 0$ the stochastic field $\mathbf{B}(t)$ responsible for the MM spin motion emanates from nuclear moments, most likely protons. Since there are many protons in the ligands, the variations between ligands do not have a big impact on τ_ϕ. According to Eq. (2), τ_ϕ on the order of 10 nsec could be generated by a field $B \sim 1$ to 0.01 G, which for $S = 10$ is equivalent to 200 to 0.2 MHz, fluctuating at a rate of $1/\tau_c \sim 4$ to 4×10^{-4} $\mu\mathrm{sec}^{-1}$, respectively. These values are typical for nuclei. In Fe_8 Morello *et al.* found nuclear $1/T_2$ on the order of 10^{-4} $\mu\mathrm{sec}^{-1}$ [21].

As we argued before, the dephasing time should be typical of high spin magnetic molecules made of transition metal ions embedded in a sea of protons. Indeed, the eight isotropic molecules reported here are different but have similar τ_ϕ. We have no *experimental* reason to believe that τ_ϕ will be substantially different in Fe_8 or Mn_4 where Δ was measured. In both cases $\Delta \sim 10^{-7}$ K for the $-S$ to S transitions [22]. The tunneling time $t_T = \hbar/\Delta \sim 7.6 \times 10^{-5}$ sec. This tunneling time is longer than the dephasing time $\tau_\phi \sim 10^{-8}$ sec in our and other [13,20] molecules. Moreover if, for example, $\beta = 0.001$ K$/$sec, then $t_z = \Delta/\beta \sim 1 \times 10^{-4}$ sec (for the same transition). This implies the order of time scales $t_Z \sim t_T \gg \tau_\phi$, a regime which corresponds to a strong dephasing. For $\beta = 0.1$ K$/$sec we have $t_T \gg t_Z \gg \tau_\phi$. As we mentioned before, the impact of the Heisenberg type stochastic fluctuations in this order of time scales on transition probabilities is not known theoretically.

To summarize, we have measured spin correlations in isotropic molecular magnets on a wide range of S values. We found that the correlation time is nearly S and ligand independent and on the order of 10 nsec. We use this time as an estimate of dephasing times in nonisotropic molecules such as Fe_8 and Mn_4 where tunneling occurs. Our findings call for a theoretical development of the LZ problem with stochastic field fluctuations coupled to all components of the spin **S** operator, where τ_ϕ is the shortest time scale in the problem.

[1] L. Thomas, F. Lionti, R. Ballou, D. Gatteschi, R. Sessoli, and B. Barbara, Nature (London) **383**, 145 (1996); J. R. Friedman, M. P. Sarachik, J. Tejada, and R. Ziolo, Phys. Rev. Lett. **76**, 3830 (1996).

[2] L. D. Landau, Phys. Z. Sov. **2**, 46 (1932).

[3] C. Zener, Proc. R. Soc. A **137**, 696 (1932).

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

[5] E. Shimshoni and A. Stern, Phys. Rev. B **47**, 9523 (1993).

[6] N. A. Sinitsyn and N. Prokof'ev, Phys. Rev. B **67**, 134403 (2003); N. A. Sinitsyn and V. V. Dobrovitski, Phys. Rev. B **70**, 174449 (2004).

[7] N. V. Prokof'ev and P. C. E. Stamp, Phys. Rev. Lett. **80**, 5794 (1998).

[8] P. C. E. Stamp and I. S. Tupitsyn, Phys. Rev. B **69**, 014401 (2004); A. Morello, P. C. E. Stamp, and I. S. Tupitsyn, Phys. Rev. Lett. **97**, 207206 (2006).

[9] W. Wernsdorfer, R. Sessoli, A. Caneschi, D. Gatteschi, and A. Cornia, Europhys. Lett. **50**, 552 (2000).

[10] J. Villain, Eur. Phys. J. B **48**, 173 (2005).

[11] E. Shimshoni and Y. Gefen, Ann. Phys. (N.Y.) **210**, 16 (1991).

[12] K. Saito, M. Wubs, S. Kohler, Y. Kayanuma, and P. Hanggi, arXiv:cond-mat/0703596 [Phys. Rev. B (to be published)]; A. T. S. Wan, M. H. S. Amin, and S. Wang, arXiv:cond-mat/0703085.

[13] A. Ardavan *et al.*, Phys. Rev. Lett. **98**, 057201 (2007).

[14] Z. Salman, A. Keren, P. Mendels, V. Marvaud, A. Scuiller, M. Verdaguer, J. S. Lord, and C. Baines, Phys. Rev. B **65**, 132403 (2002).

[15] V. Marvaud, C. Decroix, A. Scuiller, J. Vaissermann, C. Guyard, F. Gonnet, and M. Verdaguer, Chem. Eur. J. **9**, 1677 (2003).

[16] V. Marvaud, C. Decroix, A. Scuiller, J. Vaissermann, C. Guyard, F. Gonnet, and M. Verdaguer, Chem. Eur. J. **9**, 1692 (2003).

[17] V. Marvaud, J. M. Herrera, T. Barilero, F. Tuyeras, R. Garde, A. Scuiller, C. Decroix, M. Cantuel, and C. Desplanches, Monatshefte für Chemie, **134**, 149 (2003).

[18] R. Tiron, W. Wernsdorfer, F. Tuyeras, A. Scuiller, V. Marvaud, and M. Verdaguer, Polyhedron **22**, 2427 (2003).

[19] A. Keren, Phys. Rev. B **50**, 10 039 (1994).

[20] W. Wernsdorfer, A. Müller, D. Mailly, and B. Barbara, Europhys. Lett. **66**, 861 (2004).

[21] A. Morello, O. N. Bakharev, H. B. Brom, R. Sessoli, and L. J. de Jongh, Phys. Rev. Lett. **93**, 197202 (2004).

[22] W. Wernsdofer and R. Sessoli, Science **284**, 133 (1999); W. Wernsdorfer, S. Bhaduri, C. Boskovic, G. Christou, and D. N. Hendrickson, Phys. Rev. B **65**, 180403(R) (2002).