Direct measurement of the tunneling rate of the magnetization in Fe8 via $^{57}$Fe nuclear spin-lattice relaxation by strong collision.

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(Dated: March 23, 2022)

$^{57}$Fe and $^1$H relaxation measurements have been performed in single crystal and oriented powder of enriched $^{57}$Fe8 molecular cluster in the temperature range 0.05–1.7 K in zero external field and with small perturbing longitudinal field ($< 1$ T). On the basis of the experimental results it is argued that in zero external field the nuclear spin-lattice relaxation ($1/T_1$) mechanism is driven by a strong collision mechanism whereby $1/T_1$ is a direct measure of the incoherent tunneling probability in the low lying magnetic energy states of the molecular nanomagnet. The approximate value of the effective tunneling rate vs $T$ and $H$ derived directly from $1/T_1$ is shown to be consistent with theoretical estimates based on known parameters of the Hamiltonian.

Single molecule magnets (SMM) are magnetic systems formed by a cluster of transition metal ions within large organic molecules.¹,² SMM are characterized by nearly identical and magnetically isolated molecules with negligible intermolecular exchange interactions, which allows the investigation of nanomagnetism from the macroscopic measurement of the bulk sample. Recently, SMM have been paid much attention not only for the fundamental physical properties but also for the potential applications in quantum computing and data storage.³

Among the molecular magnets, Mn12ac and Fe8 clusters,⁴,⁵ which have a high total ground state spin ($S = 10$), are of particular interest due to the superparamagnetic behavior and the quantum tunneling of the magnetization (QTM) observed at low temperature due to the large uniaxial anisotropy. The octanuclear Fe$^{3+}$ cluster,⁵ (Fe8) is a particularly good candidate for the study of quantum effects since it couples an uniaxial anisotropy leading to an energy barrier of 25 K to a non negligible in-plane anisotropy. The latter is crucial in enhancing the tunneling splitting of the pairwise degenerate magnetic quantum states. In fact, Fe8 shows pure quantum regime below 0.4 K. Moreover, it was found that the enrichment of $^{57}$Fe isotope in Fe8 shortens the relaxation time demonstrating that the hyperfine field plays a key part in QTM. Together with intensive theoretical investigations,⁶,⁷,⁸,⁹,¹⁰ QTM in Fe8 has been revealed by various techniques such as magnetization measurements,¹¹,¹²,¹³ specific heat measurements,¹⁴,¹⁵,¹⁶,¹⁷,¹⁸ and nuclear magnetic resonance experiments and thus one can observe both $^1$H and $^{57}$Fe NMR in zero external field. In this low temperature region the spin dynamics is dominated by incoherent tunneling between pairwise degenerate $m$ magnetic states. In a NMR experiment performed in the local hyperfine field, whenever a tunneling event occurs, the quantization axis of the nuclear spins reverses its direction and therefore the conventional perturbative approach cannot be used to describe nuclear relaxation as first pointed out by Morello.²¹ We thus thought about applying a strong collision theory whereby the nuclear $1/T_1$ is predicted to be directly proportional to the tunneling rate. Prompted by this circumstance we have undertaken a systematic investigation of the zero field $^{57}$Fe and $^1$H NMR in Fe8 with the aim of both characterizing this very interesting and seldom observed nuclear relaxation regime and of obtaining information about the incoherent tunneling rate of the magnetization.

The formula of the molecular cluster is $[\text{Fe}_8(\text{tacn})_8\text{O}_2(\text{OH})_2]^{8+} [\text{Br}_8 \cdot 9\text{H}_2\text{O}]^{8-}$ (in short Fe8) where tacn is the organic ligand 1,4,7-triazacyclonane. Fe8 consists of eight Fe$^{3+}$ ions ($s = 5/2$) whereby the antiferromagnetic interactions among the Fe$^{3+}$ spins lead to a total spin $S = 10$ ground state.²²

The $^{57}$Fe and $^1$H NMR measurements were performed in both a sample of oriented powder and a single crystal both enriched in the $^{57}$Fe isotope. The relaxation measurements were performed by standard Fourier Transform (FT) pulse spectrometers, using a saturating radio frequency sequence of several 90° pulses and detection of the nuclear magnetization by a 90°–180° spin echo sequence. The $^{57}$Fe zero field NMR spectrum is composed of eight resonance lines.²⁰ The measurements presented here refer to the line at about 72.4 MHz for oriented powder and at about 65.6 MHz in single crystal. The $^1$H zero field NMR spectrum is also structured in a complex way. In the proton case measurements at different positions of the spectrum were performed namely at 23 MHz and 18 MHz. Temperatures from 1.5 K down
to 50 mK were obtained using both a closed cycle \(^5\)He cryostat and a \(^3\)He–\(^4\)He dilution refrigerator cryostat.

The temperature dependence of the \(^{57}\)Fe \(1/T_1\) in zero external magnetic field is plotted in Fig. 1. The main feature here is the \(T\)-independent plateau reached below 0.4 K, the same temperature at which the quantum regime is observed in magnetization measurements [5]. In Fig. 2 we show the field dependence at 1.35 K of the \(^{57}\)Fe \(1/T_1\) in oriented powder with the magnetic field applied along the main anisotropy axis \(z\). The main feature in this case is the sudden drop of the relaxation rate when a small longitudinal field is applied. Again, this is a clear indication of the presence of a contribution to relaxation due to quantum fluctuations, contribution which is removed by the small longitudinal field which prevents quantum tunneling to occur.

Before analyzing the data in Figs. 1 and 2 quantitatively we discuss the mechanism of nuclear spin-lattice relaxation by strong collision. In the case of \(^{57}\)Fe NMR in zero external field and in low fields a tunneling transition between pairwise degenerate states \(\pm m\) of the molecule results in the rapid change of the local field which is the quantization field for the \(^{57}\)Fe nuclei. In this case a sudden approximation strong collision approach should be utilized to describe the nuclear spin-lattice relaxation rate. A simple case of strong collision due to a rapid inversion of a magnetic field is illustrated in Ref. [22]. The nuclear relaxation by strong collision has been treated in details for the case of modulation of the nuclear dipolar interaction by ultra-slow diffusion motion in insulators [23] and in the case of quadrupole relaxation by a sudden change of the quantization axis as a result of a molecular reorientation [24]. Since the tunneling event occurs in a time much shorter than the nuclear Larmor frequency a non adiabatic approach is applicable and one has that the nuclear relaxation transition probability \(W\) is practically the same as the tunneling transition probability \(\Gamma\) [22, 24] i.e.:

\[
\frac{1}{T_1} = 2W = c(2\Gamma) \tag{1}
\]

where \(c\) is a constant of the order of one and \(\Gamma\) is the effective incoherent tunneling rate.

On the basis of Eq. (1) we argue that the measured \(1/T_1\) in Fig. 1 is a direct measurement of the incoherent tunneling probability \(\Gamma\). It is instructive to observe that the strong collision result [Eq. (1)] can be obtained as a limit of the weak collision result. In fact, in the weak collision case and for random fluctuations of the hyperfine field due to incoherent tunneling one has [16]:

\[
\frac{1}{T_1} = A^2 \frac{2\Gamma}{\Gamma^2 + \omega_L^2} \tag{2}
\]

where \(A\) is the average fluctuating hyperfine field at the nuclear site and \(\omega_L\) is the nuclear Larmor frequency. Eq. (2) was found to describe well the proton relaxation in FeS at high magnetic fields where the tunneling events generate a small perturbation of the effective local field i.e. \(A \ll \omega_L\) [16]. In the limit of slow motion (\(\Gamma \ll \omega_L\)) and for the case of a total change of local field i.e. \(A \approx \omega_L\) Eq. (2) does indeed reduce to the strong collision case Eq. (1). For the case of \(^{57}\)Fe NMR the local hyperfine field is directed along the magnetization of the molecule and a tunneling event corresponds to a simple reversal of the direction of the quantization field. Thus one may argue that \(A = \omega_L\) in Eq. (2) and thus in the slow motion, strong collision limit Eq. (1) and Eq. (2) coincide for \(c = 1\). On the other hand for \(^1\)H NMR a tunneling event corresponds to a change of both longitudinal and transverse components of the local hyperfine field at the proton site. This may lead to \(A\) being greater than \(\omega_L\) in Eq. (2) and \(c\) greater than one in Eq. (1). The theoretical estimate of the effect is outside the scope of this paper and thus we will treat \(c\) as an adjustable parameter in the fit of the proton data presented further on.

In order to support our claim that the nuclear relaxation rate is the direct measurement of the tunneling rate we estimate the latter on the basis of existing theories and experimental results, and compare it to \(1/T_1\). The incoherent tunneling probability can be written as [22, 26, 27]:

\[
\Gamma_{m,m'} = \frac{\Delta^2_{m,m} W_m}{(\xi + \Delta E_{m,-m})^2 + W_m^2}. \tag{3}
\]

\(\Delta_{m,m'}\) represents the tunneling splitting of the corresponding \(m\) states. \(W_m\) is a broadening parameter of the magnetic \(m\) state which includes both the lifetime
broadening due to spin-phonon interaction and the hyperfine interaction with nuclei, and $\xi$ is the longitudinal component of the internal bias field due to intermolecular dipolar interaction. Finally, $\Delta E_{m,m'}$ represents the external bias due to the application of a longitudinal field which splits the otherwise degenerate $m$ states. The measured quantity is the effective tunneling rate obtained by summing the tunneling probability for the different $m$ states weighted by the corresponding Boltzmann factor:

$$\Gamma = \sum_{m} \Gamma_{m,m'} \exp(-E_{m}/k_{B}T).$$

The tunneling splittings necessary to calculate $\Gamma$ from Eqs. 3 and 4 can be calculated from the model Hamiltonian which describes the $S=10$ magnetic ground state of the Fe8 molecular cluster:

$$\mathcal{H} = DS_{z}^{2} + E \left(S_{x}^{2} - S_{y}^{2}\right) + g\mu_{B}\mathbf{S} \cdot \mathbf{H} + D_{2}S_{z}^{4} + E_{2} \left[S_{z}^{4} \left(S_{x}^{2} - S_{y}^{2}\right)^{2} + \left(S_{x}^{2} - S_{y}^{2}\right)^{2} \right] + C \left(S_{x}^{2} + S_{y}^{2}\right),$$

where $S_{x}$, $S_{y}$, and $S_{z}$ are the three components of the total spin operator, $D$ and $E$ are the axial and the rhombic anisotropy parameter, respectively, $\mu_{B}$ is the Bohr magneton, and the last three terms are the fourth order correction terms. The tunneling splitting in the ground state was measured directly with Landau-Zener tunneling experiments and found to be $\Delta_{10} \sim 10^{-7}$ K. Thus we use in Eq. 5 the values of the parameters $D = -0.293$ K, $E = 0.047$ K, $D_{2} = 3.54 \times 10^{-5}$ K, $E_{2} = 2.03 \times 10^{-7}$ K from Ref. 23 but for $C$ we use a different value i.e., $C = -2.7 \times 10^{-5}$ K so as to obtain agreement with the experimental value of $\Delta_{10}$. Then by solving Eq. 5 we find $\Delta_{10} = 0.5 \times 10^{-7}$ K, $\Delta_{9} = 3.6 \times 10^{-6}$ K, and $\Delta_{8} = 1.3 \times 10^{-4}$ K. With the values of $\Delta_{m}$ calculated above inserted in Eqs. 3 and 4, one explains both the field dependence in Fig. 2 and the $T$-dependence in Fig. 1 with a choice of fitting parameter $W_{10} = 2.5 \times 10^{8}$ (rad Hz), $W_{9} = 7 \times 10^{9}$ (rad Hz), and $W_{8} = 9 \times 10^{10}$ (rad Hz). The parameter $\xi$ in Eq. 3 was set $\xi = 4.4 \times 10^{9}$ (rad Hz) corresponding to the correct order of magnitude for intermolecular dipolar fields [29, 30]. The broadening parameter $W_{10}$ for the ground state is in good agreement with the value measured directly by “hole digging” experiments [31]. The rapid increase of the broadening parameter $W_{m}$ for $m$ smaller than 10 is consistent with the rapid increase of the density of states of phonons, which contribute to $W_{m}$ at higher temperatures. We thus conclude that our measured $\Gamma$ is consistent with the tunneling splitting $\Delta_{10}$ and the broadening $W_{10}$ obtained from theory and different experiments. We emphasize once more that only NMR measures directly the incoherent tunneling rate $\Gamma$ while the consistency with known values of the tunneling splitting is based on Eq. 3 and is thus indirect.

We compare now the results for $^{57}$Fe NMR with our data for $^{1}$H NMR in Fig. 3. Proton relaxation data in zero field have been published earlier [17] in non enriched Fe8. Our data in enriched $^{57}$Fe8 show the same $T$-dependence but are almost a factor of two larger which
FIG. 4: Comparison of the temperature dependence of $^{57}\text{Fe}$ $1/T_1$ in Fe8 (full line) with $^{55}\text{Mn}$ $1/T_1$ in Mn12, extracted from Refs. [21, 31]. Inset shows the analogous comparison for the longitudinal field dependence. It is noted that as expected the small anomaly at the level crossing field both in Fe8 ($H_c \sim 0.22 \, \text{T}$) and Mn12 ($H_c \sim 0.5 \, \text{T}$) are observed at temperatures where the first excited states are thermally populated, and thermal assisted tunneling takes place.

should be related to the isotope effect on the tunneling rate [9]. As can be seen the results for the $T$ dependence of the proton relaxation in zero field track the ones for $^{57}\text{Fe}$ with a rescaling factor of the order of 10. This is consistent with the argument that the relaxation of both nuclei measure directly the effective tunneling rate $\Gamma$ according to Eq. (1). The multiplication factor of 10 can arise from the value of the constant $c$ in Eq. (1) which can be larger for $^1\text{H}$ NMR for the reasons discussed above.

Finally the $^{57}\text{Fe}$ relaxation data in Fe8 are compared in Fig. 4 with the $^{55}\text{Mn}$ relaxation data in Mn12 from Ref. [21]. We emphasize that the Mn12 case is more complicated than Fe8. One could reinterpret the $^{55}\text{Mn}$ relaxation data in terms of strong collision with a caveat: the $^{55}\text{Mn}$ $1/T_1$ in Mn12 is dominated by the presence of a sizeable fraction of fast relaxing molecules combined with intercluster nuclear spin diffusion as shown in Refs. [21, 31]. Thus the low $T$ plateau of $1/T_1$ in Mn12 should not be directly related to the tunneling rate of the bulk Mn12 sample but rather to a combination of the tunneling rate of the fast relaxing molecules and of the intercluster spin diffusion rate.

In conclusion, we have shown that both $^{57}\text{Fe}$ and $^1\text{H}$ nuclear relaxation in zero external field and at low temperature in molecular nanomagnet Fe8 is determined by a strong collision mechanism associated with the reversal of the magnetization due to incoherent tunneling. This finding can be generalized to other molecules under similar conditions and should thus be very valuable because it allows to measure directly through the $1/T_1$ values the effective tunneling rate in molecular nanomagnets.

We thank B.J. Suh for collaboration, A. Cornia for providing the enriched powder sample of Fe8, and L.J. de Jongh and A. Rigamonti for useful discussions. Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This work at Ames Laboratory was supported by the Director for Energy Research, Office of Basic Energy Sciences.

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