Magnetic quantum tunneling in Fe$_8$ with excited nuclei

Oren Shafir and Amit Keren
Department of Physics, Technion-Israel Institute of Technology, Haifa 32000, Israel

Satoru Maegawa and Miki Ueda
Graduate School of Human and Environmental Studies, Kyoto University, Kyoto 606-8501, Japan

Efrat Shimshoni
Department of Physics, Bar-Ilan University, Ramat Gan 52900, Israel

(Received 11 December 2009; revised manuscript received 15 February 2010; published 16 July 2010)

We investigate the effect of dynamic nuclear-spin fluctuation on quantum tunneling of the magnetization (QTM) in the molecular magnet Fe$_8$ by increasing the nuclei temperature using radio frequency (rf) pulses before the tunneling measurements. Independently we show that the nuclear-spin-spin relaxation time $T_2$ has strong temperature dependence. Hence, in principle, the rf pulses should modify the nuclear-spin dynamical. Due to very long spin-lattice relaxation time, the rf pulses do not change the electrons spin temperature. Nevertheless, we found no effect of the nuclear-spin temperature on the tunneling probability. This suggests that in our experimental conditions only the hyperfine-field strength is relevant for QTM. We demonstrate theoretically how this can occur.

DOI: 10.1103/PhysRevB.82.014419 PACS number(s): 75.50.Xx, 76.60.–k

The importance of nuclei to quantum tunneling of the magnetization (QTM) in Fe$_8$ subject to a time-dependent magnetic field was demonstrated experimentally by Wernsdorfer et al.\textsuperscript{1,2} They compared the tunneling rate of the standard Fe$_8$ sample with a deuterated sample and with a sample where $^{56}$Fe was replaced partially by $^{57}$Fe. In the regime of fast sweeping rates, where the tunneling rate was shown to be consistent with the Landau-Zener formula,\textsuperscript{3} these measurements yielded an effective tunnel splitting $\Delta$ for each sample. The enrichment with deuterium causes a decrease in $\Delta$, in accord with the decreased hyperfine field (HF).\textsuperscript{4} Similar conclusion was obtained with the $^{57}$Fe enrichment. However, the exchange of isotopes does not only vary the strength of the HF exerted on the molecule: it also changes the nuclear-spin-spin relaxation rate $T_2$. Both quantities might be important for the nuclear-assisted tunneling process.\textsuperscript{5} Isotope substitution cannot tell if only one or both quantities are relevant. Therefore, it is not yet established experimentally how exactly nuclei impact the tunneling process.

The experiment reported here aims at distinguishing between the contribution of the HF and $T_2$ to QTM. This experiment is fundamentally distinct from previous nuclear magnetic resonance (NMR) work where the influence of QTM on the nuclei was investigated.\textsuperscript{6,7} Here, we focus on the opposite effect, i.e., we manipulate $T_2$ by exciting the nuclei and examine the resulting impact on the electronic spin dynamics. To this end, we measure the magnetization of Fe$_8$ during field sweep after transmitting radio frequency (rf) at the protons resonance. This transmission raises the protons temperature without changing the electrons temperature due to the enormous proton spin-lattice relaxation time $T_1$ which is longer than 1000 s at subkelvin temperatures.\textsuperscript{7} Provided $T_2$ is dependent on the protons temperature, this procedure allows its tuning without modification of the hyperfine field. Our major finding is that QTM is not affected by the application of rf, implying that $T_2$ is not a relevant parameter, and that QTM is dependent on the HF only. We demonstrate that such a scenario is indeed possible using a simple theoretical model.

As noted above, our conclusions are based on an underlying assumption that $T_2$ is significantly dependent on the protons temperature $T$. To substantiate this assumption, we present results of a separate measurements indicating that $T_2$ decreases with increasing temperature. In principle, it is not obvious that raising the protons temperature by heating is equivalent to the application of rf. In particular, if the nuclear-spin-spin interaction is indirect, namely, it is mediated by the lattice or electrons, the $T$ dependence of $T_2$ may be caused by the $T$-dependent properties of these other degrees of freedom. We argue below, however, that such an indirect coupling mechanism is not likely to dominate the spin-spin interaction in our case. Such indirect interaction would lead to an opposite $T$ dependence, i.e., an increase in $T_2$ upon heating.\textsuperscript{8} Therefore, a direct nuclear-spin interaction seems to dominate in our case, implying that $T_2$ is dictated by the temperature of the pure nuclear-spin system.

For our experiment, a Faraday force magnetometer shown in Fig. 1 was constructed inside the inner vacuum chamber of a dilution refrigerator (DR) following the design of Sakai-ibara et al.\textsuperscript{9} with the addition of an rf coil. This magnetometer is suitable for measurements in high fields and at subkelvin temperatures with no metallic parts near the sample. This is important for minimizing the heating of metallic parts with the rf. The DR is equipped with a main superconducting magnet that produces the field $H$, and two oppositely wound superconducting magnets that produce a field gradient.

The sample is mounted on the small load-sensing device made of two parallel plates variable capacitor. The movable plate is suspended by two pairs of orthogonal crossed 0.2-mm-diameter phosphor-bronze wires attached to it with epoxy. The static lower plate was mounted on an epoxy screw for adjusting the initial capacitance $C_0$. When the sample is subjected to a spatially varying magnetic field $B$, it...
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thermal link, there is a calibrated thermometer able plate. Approximately 2 cm above the sample, on the hydrogen and is suitable for cryogenic applications. The bottom of the PCTFE, a fluorocarbon-based polymer, which has no hydrogen and is suitable for cryogenic applications. The bottom of the PCTFE is connected by a thermal link to the DR mixing chamber which produces the cooling and to the movable plate. Approximately 2 cm above the sample, on the thermal link, there is a calibrated thermometer (RuO₂ R2200) in a gold-plated casing. It is important to mention that the sample is in vacuum with no exchange gas, and therefore its temperature \( T \) is not exactly the same as the temperature of the thermometer. However, this is not a problem in our experiment since below 400 mK the magnetization jumps of Fe₈ are temperature independent.\(^{11}\)

In the magnetization experiments we apply a field of +1 T and wait until thermal equilibrium is reached. We then record the field value [Fig. 2(a)], capacitance [Fig. 2(b)], and temperature [Fig. 2(c)] as the field is swept from +1 to -1 T at a rate \( \frac{dH}{dt} = 0.5 \) T/min. While we sweep the magnetic field from positive to negative, we stop for several seconds at 0.3 T (12.71 MHz) where we transmit the rf in the form of pulses as shown in Fig. 2(d). All attempts to deliver rf at a negative field resulted in immediate magnetization jumps, hence, the choice to transmit at a positive field. During the transmission, the temperature rises by 20 mK. When the field changes sign there is a larger temperature increase of 150 mK due to eddy currents in the capacitor’s plates. None of these temperature changes are enough to generate magnetization changes. To make the measurement with and without rf as similar as possible, we stopped at 0.3 T for several seconds even when we do not transmit rf.

We first concentrate on the capacitance versus time, for a full sweep shown in Fig. 2(b). \( C(H) \) has a v shape most likely due to misplacement of the sample with respect to the center of the gradient coils, which lead to field-dependent gradient. This, however, is not relevant for the rf-dependent measurements. A closer look shows that at times where the field is positive the capacitance is a smooth function of time (and field). This is because the spins are at their ground state for all positive fields and have nowhere to tunnel to. Once the field becomes negative, clear jumps in the capacitance are observed, indicating jumps in the magnetization that are taking place when tunneling occurs between molecular-spin states. The time it takes to sweep from the end of the rf transmission to the first jump is \( \Delta t = 60 \) s. This time is much shorter than the nuclear \( T_1 \), as demonstrated in Fig. 2(d). Therefore, the nuclei are expected to be excited when the Fe₈ spins are tunneling. We avoided rf transmission at fields higher than 0.3 T and used high sweep rate in order to keep \( \Delta t \) short. Finally, Fig. 2(c) shows that magnetization jumps are accompanied by temperature spikes. These are discussed in a separate paper.\(^{12}\)

The results of measurements with and without the rf are summarized in Fig. 3. We focus on the first magnetization jump which is closest to the time of rf irradiation. The solid lines show sweeps with rf and the solid lines with symbols are sweeps without rf. We repeated these runs several times and found that within our experimental resolution, and stability between individual sweeps, no effect of the rf can be detected.

FIG. 1. (Color online) Cross-sectional view of the Faraday balance with: (1) movable plate of the capacitor, (2) screw for capacitor’s fixed plate height adjustment, (3) sample, (4) PCTFE, (5) gold-plated casing of the thermometer, (6) thermal link to the DR mixing chamber, (7) main coil, (8) gradient coils, and (9) rf coil.

FIG. 2. (Color online) The scheme of the measurements showing: (a) the magnetic field swept from positive to negative, (b) the capacitance, (c) the temperature, and (d) the rf transmission. \( \Delta t \) is the time from the transmission to the first capacitance (magnetization) jump. \( T_1 \) is the nuclear-spin-lattice relaxation time.
To appreciate this result we performed $T_2$ measurements, using a $\pi/2-\pi-\pi$ pulse sequence, inside the mixing chamber of a DR and He cryostat using a more standard NMR setup and coil. The measurements were done at fields of 0.76 T and 0.65 T and frequencies of 32 MHz and 29 MHz, respectively. At these conditions the resonance field for most of the protons is not shifted from the free proton resonance, and the linewidth $\Delta H$ is on the order of 200 mT. The results of $1/T_2$ are presented in the inset of Fig. 4. $T_2$ varies from less than $10^{-4}$ s at $T=3$ K to $10^{-3}$ s below $T=0.5$ K. Between 4 and 150 K $T_2$ is so short that no signal could be detected. Finally, due to the huge time-scale difference between $T_2$ and $T_1$ at all temperatures, it is reasonable to assume that $T_2$ is determined by direct nuclear-spin-spin coupling only. As pointed out above, indirect coupling is unlikely due to the temperature dependence of $T_2$. This coupling becomes more efficient as electronic and lattice degrees of freedom slow down upon cooling. Therefore, when indirect coupling dominates $1/T_2$ should increase on cooling as in the case of the cuprates, for example.8

In the setup with both rf and magnetization shown in Fig. 1 it is difficult to detect the proton signal due to the poor filling factor in the Helmholtz coil, the broad linewidth, and the extremely long $T_1$. However, the GE-varnish gluing the sample has relatively narrow line and shorter $T_1$. We therefore use the varnish signal at $T=140$ mK to confirm the delivery of the rf radiation to the sample, to measure the strength of the rf field $H_1$, and to test our ability to saturate the nuclear transitions. First, we measured the echo intensity as a function of applied field at constant frequency of 12.71 MHz (0.3 T) using a $\pi/2-\pi$ pulse sequence. As shown in Fig. 5(a), the full width at half maximum is only $4 \pm 0.5$ mT. A similar linewidth was found for the varnish in our standard NMR spectrometer at 5 K. This ensures that we deliver the radiation to the center of the rf coil. Second, we determined the optimal pulse length. The echo intensity as a function of the pulse length $t_{\pi/2}$ is presented in Fig. 5(b). The maximum echo intensity was found at $t_{\pi/2}=1.5 \pm 0.5 \mu$s. From $\gamma H/\hbar=\pi/2$ we calculated $H_1$ to be $24 \pm 4$ mT. Finally, we determined $T_1$, as presented in Fig. 5(c) by saturating the proton transitions with a train of pulses, and then measuring the recovery of the signal at a time $t$ using $\pi/2-\pi$ pulses. The pulse train equilibrates up and down proton spins population. We found that the GE-varnish $T_1$ is only 100 s. More importantly, Fig. 5(c) demonstrates our ability to saturate the proton transitions.

The above measurement allows us to estimate the variation in the nuclear $T_2$ at the time electronic spins are tunneling due to our rf irradiation. First, we examine how many protons we excite. Since $H_1$ is smaller than the Fe$_8$ linewidth $\Delta H$, our direct pulses excite only $H_1/\Delta H=10$% of the total number of protons. However during the transmission and after it, spin diffusion is taking place spreading the nuclear temperature among all nuclei. The diffusion coefficient $D$ is given by $D=W/r^2$, where $W$ is flip-flop rate of neighboring nuclei at distance $r$. For dipolar coupling $W=(\gamma^2\hbar/r^3)^2/(\gamma\Delta H)$, where $\gamma^2\hbar/r^3$ is the strength of the dipolar interaction and $1/\gamma\Delta H$ is a lower limit on the density

FIG. 3. (Color online) Capacitance measurements as a function of field swept from positive to negative with and without rf.

FIG. 4. (Color online) The proton spin-spin relaxation rate $1/T_2$ in Fe$_8$ on a log-log scale at the free proton resonance condition.

FIG. 5. (Color online) Echo intensity at 140 mK from the GE-varnish gluing the sample as a function of field (in frequency units), (b) pulse length, and (c) time after saturation. The solid lines are guides to the eyes.
of states. The time it takes for the heat to spread among all nuclei in a unit cell of volume $V$ is $t = V^{2/3}/D$, which is less than 10 s. Therefore, all nuclei should be warm before the first tunneling event is taking place.

Second, we evaluate by how much the irradiated nuclei cool during the time between transmission and tunneling. For this we employ the equation

$$1 - \exp(-\Delta t/T_e) \approx \Delta t/T_e,$$

where $T_{e,l}$ is the electron’s and lattice temperature (140 mK) and $T_n$ is the nuclei temperature. Immediately after the rf pulses ($\Delta t = 0$) $T_n = \infty$. As $\Delta t$ grows, $T_n$ decreases until at $\Delta t \rightarrow \infty$ it reaches $T_{e,l}$ again. This equation suggests that the nuclei temperature at the time of the tunneling is well above 3 K where $T_2$ increases by a factor 14 from its value at 140 mK. Therefore, we conclude that changing $T_2$ by an order of magnitude has no effect on the tunneling probability, for our sweep rate. Again, this conclusion is based on the reasonable assumption discussed above that warming only the nuclei to 3 K has the same effect on $T_2$ as warming the entire system to this temperature.

To demonstrate that it is conceivable to have an isotope effect, yet no dependence on $T_2$, we analyze an effective model for the dynamics of the system in the vicinity of a resonant transition between molecular spin levels $m$ and $m'$. This is essentially the Landau-Zener (LZ) problem with the addition of a transverse magnetic noise. The effective Hamiltonian, describing a spin $1/2$ with a resonance tunnel splitting $\Delta$, subject to a time-dependent magnetic field in the $z$ direction and a fluctuating magnetic field in the $x$ direction, is given by

$$\mathcal{H} = \alpha z S_z + \Delta S_x + B_x(t)S_x,$$

Here $S_x = \frac{1}{2}\sigma_x$ and $S_y = \frac{1}{2}\sigma_y$, where $\sigma_x$ and $\sigma_y$ are the Pauli matrices and $\alpha$ is related to the sweeping rate of the field $H$ via

$$\alpha = 2g\mu_B(m - m')dH/dt.$$  

$\Delta$ is determined by many factors such as magnetocrystalline anisotropy, electron-dipolar fields, transverse fields due to sample misalignment, etc. We assume that the stochastic field $B_x(t)$ has a correlation function

$$\langle B_x(t)B_x(t') \rangle = \langle B_x^2 \rangle \exp(-|t - t'|/\tau_e),$$

where $\langle \rangle$ stands for an average of stochastic field realizations; $B_x^2$ is related to the hyperfine field (see below), and for nuclear noise the correlation time $\tau_e$ stands for $T_2$. We consider only a transverse fluctuating field since for the $-10$ to $9$ transition, the measured $\Delta \sim 10^{-7}$ K, and our sweep rate, the sudden limit is obeyed, namely, $\Delta/\sqrt{\alpha} \ll 1$. In this case it is well established that a stochastic field coupled to the $z$ direction of the spin has no effect on the LZ tunneling probability.

We next write the wave function as $\Psi(t) = \tilde{C}_-^\dagger(t)\tilde{C}_+(t) + \tilde{C}_+(t)\tilde{C}_-^\dagger(t)$, where $|\pm\rangle$ denote eigenstates of $\sigma_z$. Defining $C_\pm(t) = \exp(\pm i\alpha^2/4\hbar)\tilde{C}_\pm(t)$ and introducing a dimensionless time variable $y = t/\alpha^2/\hbar$, the Schrödinger equation can be expressed in the integral form

$$C_\pm(\infty) = \frac{i}{2\sqrt{\alpha^2/\hbar}} \int_{-\infty}^{\infty} [\Delta + B_x^2(y)] e^{-y^2/2} C_\pm(y) dy.$$  

Assuming the initial conditions $C_+(\pm\infty) = 1$ and $C_-(\pm\infty) = 0$, the tunneling probability is given by $P = |\langle C_-(\infty) | C_+(\infty) \rangle|^2$. In the sudden limit, $C_+$ does not change much. Assuming in addition that the fluctuating field is weak such that $B_x \ll \sqrt{\alpha^2/\hbar}$, one can replace $C_+$ under the integral by 1 to first order in $\Delta$ and $B_x$. This yields

$$P = \frac{1}{4\alpha^2/\hbar} \int_{-\infty}^{\infty} dxdy(\Delta^2 + B_x^2) e^{-y^2/2} e^{i(x^2 - y^2)/2},$$

where we have used Eq. (4) with $\nu = 1/\tau_e/\alpha^2/\hbar$.

This results in a simple expression for the tunneling rate

$$P(\Delta, B_x^2) = \pi(\Delta^2 + B_x^2)/2\alpha^2/\hbar,$$

in which there is no dependence on the parameter $\nu$. The transition probability is therefore dependent on the HF strength but not on its correlation time $\tau_e$. It can be cast as $P = \pi\Delta_{eff}/2\alpha^2/\hbar$, where $\Delta_{eff} = \sqrt{\Delta^2 + B_x^2}$ can be identified with the measured tunnel splitting.

The above model is consistent with the experimental system provided $(B_x^2)^{1/2}$ is on the order of the measured tunnel splitting. When converting the Fe\textsubscript{8} problem to the two-level LZ problem, $B_x^2$ is scaled down from the field $B_x$ the nuclei produce, since $B_x$ has a matrix element between $m$ and $m'$ states only in the $|m - m'|$th order of perturbation theory. As a consequence, Garanin and Chudnovsky\textsuperscript{17} showed that

$$B_x^2 = \frac{2D}{(m - m' + 1\cdot 2)^2} \frac{(S + m')!(S + m)!}{(S - m')!(S + m)!} \left\langle B_x^2 \right\rangle_{m - m'},$$

where $D = 0.27$ K is the Fe\textsubscript{8} single-ion anisotropy coefficient. Protons produce a field on the order of $1-10$ mT inside a solid, corresponding to $B_x$ of 0.01–0.001 K, which is not small. However, in our case $m - m'$ is 19 therefore $B_x^2$ is practically zero. For $B_x^2$ to be of order $10^{-7}$ K, there has to be a shortcut in the tunneling process such that the relevant $m - m'$ is around 6–7. It is reasonable that such a shortcut exists since we, and other researchers,\textsuperscript{15} see only four magnetization jumps and not 10.

To summarize, we exploit the strong temperature dependence of the nuclear-spin-spin relaxation time $T_2$ around 1 K in order to test the effect of nuclear fluctuations on quantum tunneling of the magnetization. Since in our case $T_2$ is most likely a property internal to the nuclear-spin system, we change it by warming only this system with radio frequency transmitted at the protons resonance. We then measure the size of the magnetization jumps due to tunneling. During the magnetization measurements the nuclei stay warm due to the enormously long spin-lattice relaxation time $T_1$. We found no effect of the nuclear-spin temperature on the magnetization jump and conclude that the parameter $T_2$ is irrelevant to...
the tunneling probability in our experimental conditions. We present a calculation demonstrating that nuclear spins can, indeed, affect the tunneling via their hyperfine-field strength only.

We are grateful for RBNI Nevet program and Israeli ministry of science “Tashtiot” program for supporting this research. E.S. was supported by the Ministry of Science and Technology (Grant 3-5792).

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