Magnetic quantum tunneling in Fe_8 with excited nuclei

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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 dynamic. 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.

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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.*[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,[3] these measurements yielded an effective tunnel splitting Δ for each sample. The enrichment with deuterium causes a decrease in Δ, in accord with the decreased hyperfine field (HF).[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.[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.[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.[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.[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 Sakakibara *et al.*[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

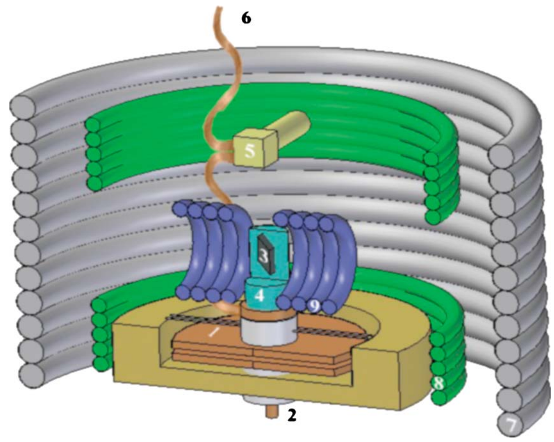

FIG. 1. (Color online) Cross-sectional view of the Faraday balance with: (1) movable plate of the capacitor, (2) screw for capacitor's fixed plate height adjustment, (3) sample, (4) PCTFE, (5) gold-plated casing of the thermometer, (6) thermal link to the DR mixing chamber, (7) main coil, (8) gradient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

will experience a force $\mathbf{F}=M_z(\partial B_z/\partial z)\hat{z}$. This force is balanced by the wires. The displacement of the plate is proportional to F and can be detected as a capacitance C change. The total capacitance response is then given by

$$C_0^{-1} - C^{-1} = a \cdot M_z(\partial B_z/\partial z), \tag{1}$$

where a is a constant that depends on the elastic properties of the wires.

The sample is grown by the method described in Ref. 10 and is 20 mm^3. It is oriented with its easy axis parallel to the magnetic field H. The alignment is done manually at room temperature using the distinct facets of Fe_8. The sample is glued with GE varnish to poly-chloro-trifluoro-ethylene (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 (RuO_2 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 Fe_8 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 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.

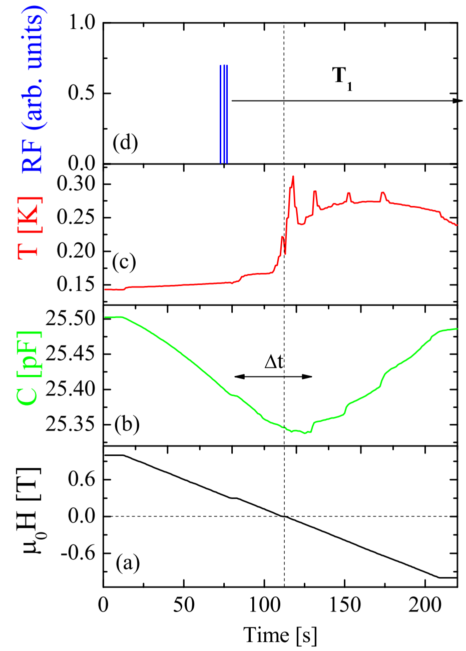

FIG. 2. (Color online) The scheme of the measurements showing: (a) the magnetic field swept from positive to negative, (b) the capacitance, (c) the temperature, and (d) and the rf transmission. Δt is the time from the transmission to the first capacitance (magnetization) jump. T_1 is the nuclear-spin-lattice relaxation time.

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 wheret he 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 Δt=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 Fe_8 spins are tunneling. We avoided rf transmission at fields higher than 0.3 T and used high sweep rate in order to keep Δt 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.

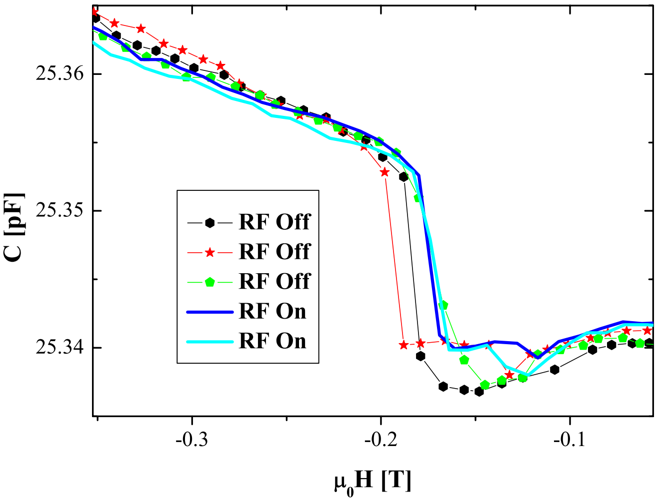

FIG. 3. (Color online) Capacitance measurements as a function of field swept from positive to negative with and without rf.

To appreciate this result we performed T_2 measurements, using a $\pi/2$-τ-π 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 ΔH is on the order of 200 mT.[13] 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 done upon cooling. Therefore, when indirect coupling dominates $1/T_2$ should increase on cooling as in the case of the cuprates, for example.[8]

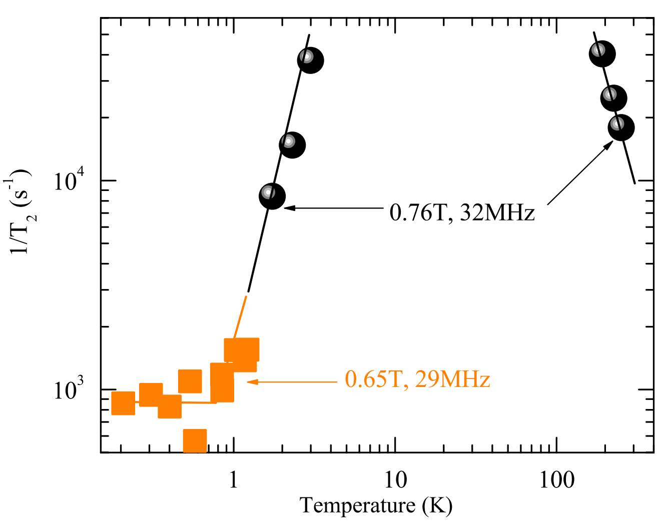

FIG. 4. (Color online) The proton spin-spin relaxation rate $1/T_2$ in Fe_8 on a log-log scale at the free proton resonance condition.

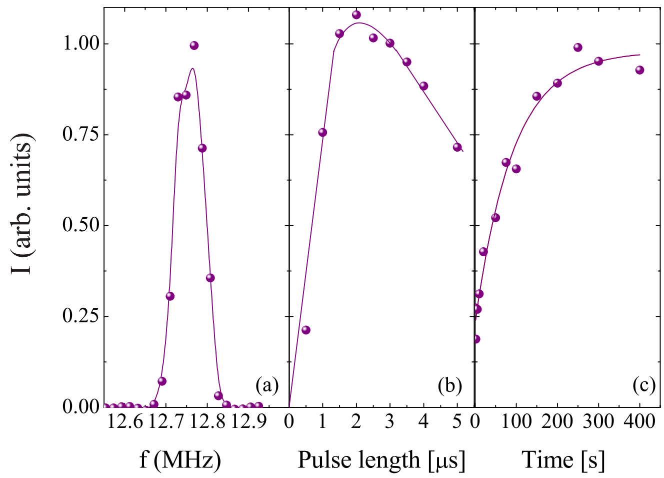

FIG. 5. (Color online) Echo intensity at 140 mK from the GE-varnish gluing the sample as a (a) function of field (in frequency units), (b) pulse length, and (c) time after saturation. The solid lines are guides to the eyes.

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 $\pi/2$-π pulse sequence. As shown in Fig. 5(a), the full width at half maximum is only 4 ± 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 $t_{\pi/2}=1.5\pm0.5$ μs. From $\gamma H_1 t_\pi=\pi/2$ we calculated H_1 to be 24 ± 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 $\pi/2$-π 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 ΔH, 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 $D=Wr^2$, where W is flip-flop rate of neighboring nuclei at distance r.[14] 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 of states.[14] The time it takes for the heat to spread among all nuclei in a unit cell of volume V is $V^{2/3}/D$, 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

$$\frac{1}{T_{e,l}}[1-\exp(-\Delta t/T_1)]=\frac{1}{T_n}, \tag{2}$$

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 Δt grows, T_n decreases until at $\Delta t\to\infty$ 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 Δ, subject to a time-dependent magnetic field in the z direction and a fluctuating magnetic field in the x direction, is given by

$$\mathcal{H}=\alpha t S_z+\Delta S_x+B_x^e(t)S_x. \tag{3}$$

Here $S_x=\frac{1}{2}\sigma_x$ and $S_z=\frac{1}{2}\sigma_z$, where σ_x and σ_z are the Pauli matrices and α is related to the sweeping rate of the field H via

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

Δ 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 $B_x^e(t)$ has a correlation function

$$\langle B_x^e(t)B_x^e(t')\rangle=\langle B_x^{e2}\rangle\exp(-|t-t'|/\tau_c), \tag{4}$$

where $\langle\ \rangle$ stands for an average of stochastic field realizations; B_x^e is related to the hyperfine field (see below), and for nuclear noise the correlation time τ_c stands for T_2. We consider only a transverse fluctuating field since for the -10 to 9 transition, the measured $\Delta\sim10^{-7}$ K,[15] and our sweep rate, the sudden limit is obeyed, namely, $\Delta/\sqrt{\hbar\alpha}\ll1$. 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.[16]

We next write the wave function as $\Psi(t)=\tilde{C}_-(t)|-\rangle+\tilde{C}_+(t)|+\rangle$, where $|\pm\rangle$ denote eigenstates of σ_z. Defining

$$C_\pm(t)=\exp(\pm i\alpha t^2/4\hbar)\tilde{C}_\pm(t)$$

and introducing a dimensionless time variable $y=t\sqrt{\alpha/\hbar}$, the Schrödinger equation can be expressed in the integral form

$$C_\mp(\infty)=\frac{i}{2\sqrt{\alpha\hbar}}\int_{-\infty}^{\infty}[\Delta+B_x^e(y)]e^{\pm iy^2/2}C_\pm(y)dy. \tag{5}$$

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

$$P=\frac{1}{4\alpha\hbar}\int_{-\infty}^{\infty}\int dxdy(\Delta^2+\langle B_x^{e2}\rangle e^{-\nu|x-y|})e^{i(y^2-x^2)/2}, \tag{6}$$

where we have used Eq. (4) with $\nu\equiv1/\tau_c\sqrt{\alpha/\hbar}$. This results in a simple expression for the tunneling rate

$$P=\pi(\Delta^2+\langle B_x^{e2}\rangle)/2\hbar\alpha, \tag{7}$$

in which there is *no dependence* on the parameter ν. The transition probability is therefore dependent on the HF strength but not on its correlation time τ_c. It can be cast as $P=\pi\Delta_{eff}^2/2\hbar\alpha$, where $\Delta_{eff}\equiv\sqrt{\Delta^2+\langle B_x^{e2}\rangle}$ can be identified with the *measured* tunnel splitting.

The above model is consistent with the experimental system provided $\langle B_x^{e2}\rangle^{1/2}$ is on the order of the measured tunnel splitting. When converting the Fe_8 problem to the two-level LZ problem, B_x^e 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[17] showed that

$$B_x^e=\frac{2D}{(m'-m-1)!^2}\sqrt{\frac{(S+m')!(S-m)!}{(S-m')!(S+m)!}}\left(\frac{B_x}{2D}\right)^{m'-m}, \tag{8}$$

where $D=0.27$ K is the Fe_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 $m'-m=19$ therefore B_x^e is practically zero. For B_x^e 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,[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.

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