Suppression of quantum phase interference in the molecular magnet Fe_8 with dipolar-dipolar interaction

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Renormalized tunnel splitting with a finite distribution in the biaxial spin model for molecular magnets is obtained by taking into account the dipolar interaction of enviromental spins. Oscillation of the resonant tunnel splitting with a transverse magnetic field along the hard axis is smeared by the finite distribution, which subsequently affects the quantum steps of the hysteresis curve evaluated in terms of the modified Landau-Zener model of spin flipping induced by the sweeping field. We conclude that the dipolar-dipolar interaction drives decoherence of quantum tunneling in the molecular magnet Fe_8, which explains why the quenching points of tunnel splitting between odd and even resonant tunneling predicted theoretically were not observed experimentally.

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Macroscopic quantum phenomena in magnetic molecular clusters have been an attractive field of research in recent years.[1–8] Octanuclear iron(III) oxo-hydroxo cluster Fe_8 is of special interest because it shows not only regular steps in the hysteresis curve but also oscillation of the tunnel splitting due to quantum phase interference.[3] Oscillation of tunnel splitting of the ground state with respect to the external field along the hard axis was predicted theoretically by Garg[4] as a consequence of the quantum phase interference of tunnel paths, and it was subsequently generalized to tunneling at excited states and resonant tunneling for the quantum transition between different quantum states with its x component of the spin $S_x=-10$ and $10-n$ (along the easy axis of Fe_8) recently.[6] The quenching points between even and odd n have a shift $\pi/2$. However, a serious problem—why the theoretically predicted shift of quenching points of tunnel splitting between odd and even resonant tunneling was not observed in the experimental hysteresis curves,[3,6,9]—remains to be solved. This is the main motivation of this paper. Here we use the Landau-Zener model[3,8–10] to describe the spin flipping induced by the sweeping field with a modified bare tunnel splitting considering the dipolar interaction with environmental spins. There are two basic interactions to be considered: spin-phonon and spin-spin interactions. For the molecular magnets Fe_8 in the mK temperature region, the spin-phonon interaction[8] can be safely ignored as the spin-lattice relaxation time is extremely long.[11] The interaction between the big spin and the environmental spins was considered as the main source of decoherence of tunneling in magnetic macromolecules[12] and recently it was shown that the nuclear spin plays an important role in magnetic relaxation.[13,14] In this paper, starting from the mean-field approximation, the dipolar interaction is treated as a local stray field $\vec{h}$ (see the following) with a Gaussian distribution. The tunnel splitting in the Landau-Zener transition rate should be considered as an average over the local stray field $\vec{h}$. In doing so we find that the quenching of the tunneling due to quantum interference is suppressed by the local stray field, and the steps in the hysteresis curve corresponding to odd resonant tunneling are understood.

We start with the biaxial spin model for the molecular magnets Fe_8.[3–5] The Hamiltonian is given by[15]

$$H=K_1S_z^2+K_2S_y^2-g\mu_B\mathbf{S}\cdot(\mathbf{B}+\vec{h}), \tag{1}$$

where $K_1>K_2>0$ and $\mathbf{B}$ is the external magnetic field. The term $-g\mu_B\mathbf{S}\cdot\vec{h}$ is the dipolar-dipolar interaction between the magnetic molecular cluster and the environmental spins, i.e., $\vec{h}=\Sigma_jJ_{ij}\mathbf{S}_j$, where the summation runs over the neighboring clusters. Strictly speaking, this should be a many-body problem. In this paper, $\vec{h}$ is treated approximately as a local stray field, $\vec{h}=\Sigma_jJ_{ij}\langle\mathbf{S}_j\rangle$. Both experimental[14] and the Monte Carlo studies[16,17] show that $\vec{h}$ has a random distribution with a distribution width in proportion to $(1-|M|)$ and its mean value proportional to M where M is the total magnetization of the system. Here we assume that $\vec{h}$ has a Gaussian distribution with an equal distribution width in all directions:[18]

$$P(\vec{h})=\frac{1}{(2\pi\sigma^2)^{3/2}}\exp[-(\vec{h}-\vec{h}_0)^2/2\sigma^2]. \tag{2}$$

To simulate the experimental setup,[3] the external magnetic field is taken to be $\mathbf{B}=\{B_x,0,B_z\}$: a uniform field B_z along the hard axis and the sweeping field B_x on the easy axis $B_x=n\Delta B\pm ct$ where n is an integer, ΔB is the field interval between neighboring resonant tunneling, and $c=dB_x/dt$. In the following calculation, we take $K_1=0.310$ K, $K_2=0.229$ K, and $c=0.1$ T/sec for the molecular magnets Fe_8.[3]

Theoretically, quantum tunneling for a spin system without a local stray field can be understood in the instanton method,[4–6] the Landau-Zener model,[8–10] and by diagonalizing the Hamiltonian numerically.[3,19] The instanton method can give the tunnel splitting. When the field along the easy axis satisfies the resonant condition $B_x+h_x=n\Delta B$, the transition rate, while the field on the easy axis sweeps over the resonant point, is given by the Landau-Zener transition formula,[8–10] $P_{LZ}=1-\exp(-\pi\Delta_n^2/\nu_n)$, where Δ_n is the tunnel splitting and $\nu_n=2g\mu_B\hbar(2s-n)c$. It should be noted that in this way we have assumed tacitly that the tunnel splitting for all spins inside the resonant window are the *same* and thus all spins tunnel with the *same* transition rate. However, when the local stray field due to the dipolar-dipolar interaction is taken into account, such a picture should be modified. A random distribution of local stray fields like Eq. (2) with a distribution width $\sigma\sim0.05$ T typical for the molecular magnets Fe_8 will block the resonant tunneling of either the ground state or the low-lying excited states.[13] Nevertheless, such a problem can be circumvented by using a sweeping field along the easy field. When B_x sweeps over the resonant point, it will make the spins with different h_x's satisfy the resonant condition and allows continuous relaxation. Since the tunnel splitting is very sensitive to the transverse local fields B_z+h_z, and h_y,[4–6] the spins tunnel with *different* tunnel splitting while B_x is sweeping over the resonant point. Consequently, the spin transition rate observed in the experiment should be given by

$$\langle P_{LZ}\rangle\simeq1-\exp\{-\pi\langle\Delta_n^2\rangle/\nu_n\}, \tag{3}$$

where $\langle\cdots\rangle$ represents the average over the distribution of the local stray field, i.e., $\langle\Delta_n^2\rangle=\int\Delta_n^2(\vec{h})p(\vec{h})d\vec{h}$. Accordingly, the tunnel splitting extracted from the measured transition rate should be $\sqrt{\langle\Delta_n^2\rangle}$ but not Δ_n. In other words, the starting point to understand the experimental observation should be $\sqrt{\langle\Delta_n^2\rangle}$ instead of Δ_n. The two quantities are qualitatively different from each other as we shall show in the following.

The instanton method[4–6] is efficient and powerful to evaluate the tunnel splitting Δ_n. The Lagrangian for the biaxial model, Eq. (1), is

$$L(\mathbf{n})=-s\hbar(1-\cos\theta)\dot{\phi}-\langle\mathbf{n}|H|\mathbf{n}\rangle, \tag{4}$$

where $|\mathbf{n}\rangle$ is the spin-coherent state. With the help of the mapping technique, $(\phi,p=s\hbar\cos\theta)$ is regarded as a pair of canonical variables. To calculate the excited-state tunneling or resonant tunneling, one needs to apply the Bohr-Sommerfeld quantization rule $\oint p\,d\phi=n\hbar$ to define the classical orbits (n is an integer). Then a propagator with both imaginary and real time will be used to describe the tunneling between two degenerate states,

$$K(n_f,T/2;n_i,-T/2)=\langle n_f|e^{iHT/\hbar}|n_i\rangle =\int d\Omega\exp\left[\frac{i}{\hbar}\int_{-T/2}^{T/2}L(\mathbf{n})dt\right]. \tag{5}$$

The tunnel splitting is found by integrating over two degenerate classical orbits. In molecular magnets Fe_8 the local stray field is rather weak, i.e., $g\mu_B|\vec{h}|/(K_2s)\ll1$. We calculate the tunnel splitting at the nth resonant tunneling point with the transverse field B_z+h_z and h_y and obtain that

$$\Delta_n\approx\frac{Q_n}{2}e^{-S_c^n}\{|e^{2qh_y}+e^{-2qh_y}+2\cos[2(s\pi-n\pi/2-d_nh_z-d_nB_z)]|\}^{1/2}, \tag{6}$$

where S_c^n is the instanton action,

$$S_c^n=\int_0^{\pi-\phi_n}d\phi\sqrt{\frac{V(\phi)-E_n}{K_1(1-\lambda\sin^2\phi)+(g\mu_Bn\Delta h/s)\cos\phi}}, \tag{7}$$

$$V(\phi)=K_2s^2\sin^2\phi-g\mu_Bn\Delta hs\cos\phi-\frac{[g\mu_B(h_z+B_z)]^2}{2K_1(1-\lambda\sin^2\phi)+2(g\mu_Bn\Delta h/s)\cos\phi}, \tag{8}$$

E_n is the energy of the nth excited state, ϕ_n is the turning point determined by $V(\pi-\phi_n)=E_n$, Q_n is the prefactor,

$$Q_n\simeq4\pi/\sqrt{V''(0)(2K_1+g\mu_Bn\Delta h/s)}, \tag{9}$$

$q=g\mu_B\pi\lambda^{1/2}/2K_2(1-\lambda)^{1/2}$, $\lambda=K_2/K_1$, and

$$d_n=\frac{g\mu_B}{2K_1}\int_0^{\pi}\frac{d\phi}{1-\sin^2\phi-\frac{g\mu_B}{2K_2s}n\Delta h\cos\phi}. \tag{10}$$

Using the parameters in Fe_8, it is found that the contribution from h_y and h_z to S_c^n and thus $Q_ne^{-S_c^n}$ is very small under the condition $g\mu_B|\vec{h}|/(K_2s)\ll1$. The average value of Δ_n^2 is given by

$$\langle\Delta_n^2\rangle\approx\frac{Q_{n0}^2}{4}e^{-2S_{c0}^n}\{e^{2q^2\sigma^2}(e^{2qh_0}+e^{-2qh_0})+2e^{-2d_n^2\sigma^2}\cos[2(s\pi-n\pi/2-d_nh_0-d_nB_z)]\}, \tag{11}$$

where $Q_{n0}=Q_n(h_z=h_y=0)$, and $S_{c0}^n=S_c^n(h_z=h_y=0)$. In the absence of a stray field, i.e., $\sigma=h_0=0$, the above expression reduces to

$$\sqrt{\langle\Delta_n^2\rangle}|_{\sigma=h_0=0}=\Delta_n(h_x=h_y=0) =Q_{n0}e^{-S_{c0}^n}|\cos(s\pi-n\pi/2-d_nB_z)|, \tag{12}$$

which indicates the oscillation of the tunnel splitting with the transverse field and a shift $\pi/2$ of quenching point between the odd and even resonant tunneling, recovering the results in the previous works.[3–6] This is known as a result of the quantum interference of the tunneling along two different paths. The qualitative difference between $\sqrt{\langle\Delta_n^2\rangle}$ and $\Delta_n(h_x=h_y=0)$ can now be seen by comparing Eq. (12) with Eq. (11). In the case of $B_z=0$ and integer spin, Eq. (12) predicts that odd-n resonant tunneling quenches due to the quantum interference, while in the presence of the stray field, Eq. (11), gives nonzero tunnel splitting,

TABLE I. Tunnel splitting $\sqrt{\langle \Delta_n^2 \rangle}$ (the unit is kelvin) for Fe_8 in the case of $B_z = h_0 = 0$.

n	$\sigma = 0.0$ T	$\sigma = 0.02$ T	$\sigma = 0.05$ T	$\sigma = 0.08$ T
0	8.399×10^{-10}	8.547×10^{-10}	1.087×10^{-9}	2.312×10^{-9}
1	0.0	2.459×10^{-9}	3.266×10^{-9}	6.450×10^{-9}
2	3.414×10^{-8}	3.473×10^{-8}	4.418×10^{-8}	9.393×10^{-8}
3	0.0	2.399×10^{-7}	3.187×10^{-7}	6.293×10^{-7}
4	2.015×10^{-6}	2.050×10^{-6}	2.608×10^{-6}	5.544×10^{-6}
5	0.0	9.878×10^{-6}	1.312×10^{-5}	2.591×10^{-5}
6	6.224×10^{-5}	6.333×10^{-5}	8.055×10^{-5}	1.713×10^{-4}

$$\sqrt{\langle \Delta_n^2 \rangle_q} \simeq \frac{\sqrt{2}}{2} Q_{n0} e^{-S_{c0}^n} \sqrt{e^{2q^2\sigma^2} - e^{-2d_n^2\sigma^2}}, \tag{13}$$

for $h_0 = 0$. The quenching due to the quantum interference is suppressed by the local stray field. In another word the quantum tunneling for odd n is decoherenced because of the dipolar interaction with the environmental spins. The tunnel splittings of all six resonant tunnelings for the molecular magnets Fe_8 with and without a local stray field are shown in Table I. We see that $\sqrt{\langle \Delta_n^2 \rangle}$ for an odd n increases from zero while the random field becomes stronger. The random field also increases the tunnel splitting of even resonant tunneling. It increases about 2.7 times as σ becomes as large as 0.08 T, which resolves the puzzle that the experimental observation is about 3.0 times larger than the numerical result for the tunnel splitting.[3] A detailed evolution of the tunnel splitting with the distribution width around the topological quenching points is shown in Fig. 1. As the width of the distribution is proportional to $(1-|M|)$, the calculated results for different M are shown in Fig. 1, which are in good agreement with the experimental observation (see Fig. 10 in Ref. 20). One can see from Eq. (11) that the main effect of h_0 is to provide an initial phase and thus shifts the oscillation. For Fe_8, $h_0 \simeq \sigma/4$,[16] and the effect of modification for nonzero h_0 is almost omissible.

The oscillation of the tunnel splitting for $s=10$ with various distribution width σ's is shown in Fig. 2. From Fig. 2, it is shown that the oscillation of the tunnel splitting due to quantum interference is suppressed by the local stray field $\vec{h}$. For a distribution width $\sigma = 0.05$ T which is estimated for Fe_8,[9,13] the oscillation of tunnel splitting with respect to the field along the hard axis is still visible, while the oscillation is suppressed completely for the width as large as 0.08 T. In fact, when the distribution width approaches the half oscillation period, the oscillation due to quantum interference disappears and the classical behavior—i.e., tunnel splitting increases monotonously with B_z—is resumed. The above analysis leads to a decoherence mechanism for quantum interference due to the dipolar-dipolar interactions between the spins without dissipation.[12]

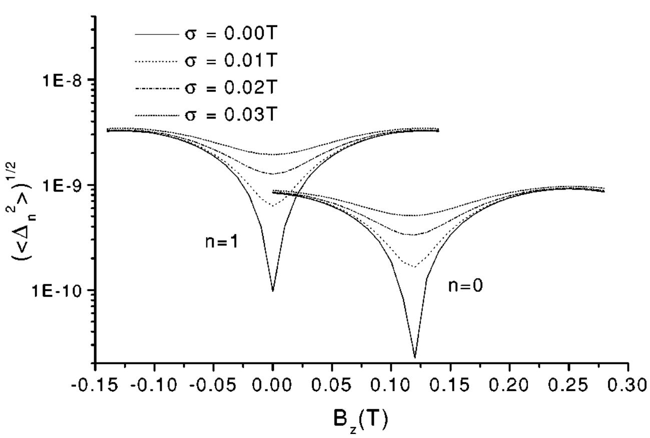

FIG. 1. Illustration of $\sqrt{\langle \Delta_n^2 \rangle}$ $(n=0,1)$ around topological quenching points due to quantum interference with different distribution width σ's.

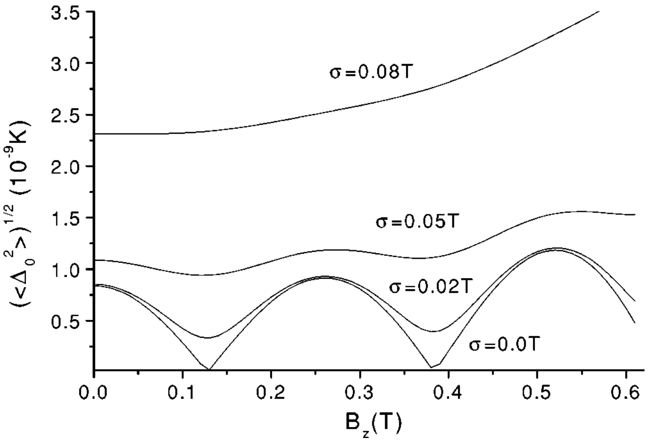

FIG. 2. The oscillation of $\sqrt{\langle \Delta_0^2 \rangle}$ with different distribution width σ's for $s=10$. From top to bottom: $\sigma = 0.08$ T, 0.05 T, 0.02 T, and 0.0 T.

The magnetization jump from the spin flipping at resonant tunneling can be calculated from the modified Landau-Zener transition rate given in Eq. (3). In principle the time evolution of the spin system in Eq. (1) can be obtained by solving the time-dependent Schrödinger equation $i\hbar(\partial/\partial t)|\Phi\rangle = H|\Phi\rangle$, which contains a set of $(2s+1)$ coupled differential equations for the model in Eq. (1). It was shown[19] that the coupled differential equations can be reduced to that of an effective two-level system with the effective Hamiltonian. Here we have

$$H_{\text{eff}}(t) = \begin{pmatrix} -(10-n)g\mu_B ct & \sqrt{\langle \Delta_n^2 \rangle}/2 \\ \sqrt{\langle \Delta_n^2 \rangle}/2 & 10g\mu_B ct \end{pmatrix}, \tag{14}$$

near the resonant condition, and the time-dependent state is given by $|\Phi_{\text{eff}}\rangle = a_{-10}(t)|-10\rangle + a_{10-n}(t)|10-n\rangle$. The tunneling splitting in Eq. (14) is $\sqrt{\langle \Delta_n^2 \rangle}$ instead of Δ_n as we discussed. Correspondingly, the magnetization jump from the nth resonant tunneling is obtained as

$$\Delta M_n = \langle \Phi_{\text{eff}}|S_x|\Phi_{\text{eff}}\rangle|_{t=+\infty} - \langle \Phi_{\text{eff}}|S_x|\Phi_{\text{eff}}\rangle|_{t=-\infty}. \tag{15}$$

Numerical results are shown in Fig. 3. It is worth emphasizing that the resulting jump is modified as a rather smooth one due to the local stray field. The hysteresis curves in Fig. 3 are drawn with the initial condition of $S_x = -10$, i.e., $a_{-10}(t=-\infty)=1$. As is shown in Fig. 3 the steps in the hysteresis

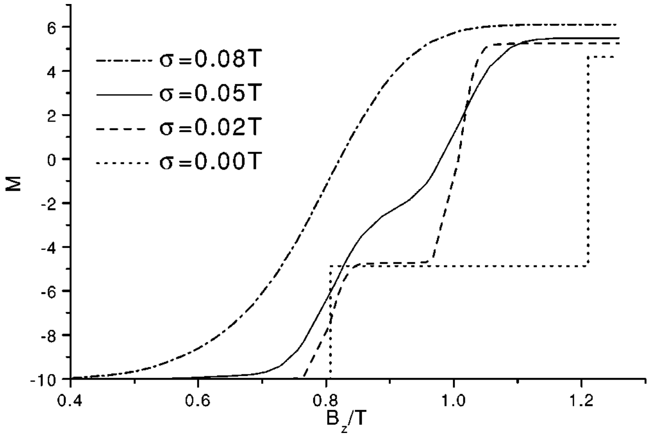

FIG. 3. Hysteresis curves with different distribution width σ's.

curve are smeared gradually with increasing the distribution width of the local stray field and the observed curve in experiment[3,9] can be recovered from the present theory.

In this paper, the local stray field is treated as a "frozen" one inside the resonant window. Strictly speaking, both the width and mean value of the distribution of the field should vary with the time-dependent magnetization during the resonant tunneling. However, it should be noted that a "frozen" distribution is based on the validity of the Landau-Zener model. If the spins "feel" the change of the local field due to spin flipping, the spin transition rate is no longer the one in Eq. (3). In that case, one should consider the nonlinear Landau-Zener tunneling[21] and the "hole-digging" mechanism.[13,14] This indicates that our result is valid when the field sweeping rate is not too small such that the evolution of the local field is relatively slower than the sweeping field. Namely, the overlap time of two levels in resonance $\tau_1 \sim \Delta_n/(2\mu_B Sc)$ should be less than the characteristic relaxation time τ_2 due to the dipolar-dipolar interaction. This means that the field sweeping rate $c > c_0 \sim \Delta_n/(2\mu_B Sc\tau_2)$. In Fe_8,[14,16] the ground-state tunneling $\Delta_0 \sim 10^{-7}$ K, $\tau_2 \sim 10^{-5}$ sec, and c_0 is estimated to be 10^{-3} T/sec., which is in good agreement with the experimental condition.[3,20] On the other hand, a finite distribution of tunnel splitting due to the local stray field has a deeper impact on the magnetic relaxation. If all the spins tunnel with the same tunneling rate, the magnetic relaxation should obey the exponential law, i.e. $e^{-\Gamma t}$ where $\Gamma = 2P_{LZ}c/A$, where A is amplitude of the ac field used in the experiment.[20] Instead, in the present picture, there is a finite distribution of tunnel splitting $p(\Delta_n)$ which will lead to a finite distribution of the relaxation rate $p(\Gamma)$ characteristic of a complex system like spin glass.[22] Consequently the resulting relaxation will obviously deviate from the simple exponential law as observed in the experiment.[20] Further analysis will be provided elsewhere.

We have studied the effect of dipolar interaction between giant spins in the molecular magnets Fe_8 in the mean-field approximation which leads to a Zimman term of the spin in a local stray field. Our main observation is that the topological quench due to the quantum phase interference of tunnel paths is suppressed by the finite distribution of the local stray field and the steps in the hysteresis curve corresponding to odd resonant tunneling are explained theoretically. Thus we conclude that the dipolar-dipolar interaction leads to the decoherence of quantum tunneling in Fe_8. Finally it is worth pointing out that the mechanism of decoherence may not be just limited in Fe_8, but can be generalized to other molecular magnets such as Mn_{12} since the local stray field due to the dipolar-dipolar and hyperfine interactions always exists.

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