Landau Zener method to study quantum phase interference of Fe$_8$ molecular nanomagnets

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We present details about an experimental method based on the Landau Zener model which allows to measure very small tunnel splittings $\Delta$ in molecular clusters Fe$_8$. The measurements are performed with an array of micro-SQUIDs. The observed oscillations of $\Delta$ as a function of the magnetic field applied along the hard anisotropy axis are explained in terms of topological quantum interference of two tunnel paths of opposite windings. Transitions between $M = -S$ and $(S-n)$, with $n$ even or odd, revealed a parity (symmetry) effect which is analogous to the suppression of tunneling predicted for half integer spins. This observation is the first direct evidence of an alternative mechanism between the only populated 10 states which are analogous to the parity effect between systems with half integer or integer spins [1]. An alternative explanation in terms of intermediate spin was also presented [2]. Hence, molecular chemistry had a large impact in the research of quantum tunneling of magnetization at molecular scales.

![Figure 1](image-url)  
**FIG. 1.** Schematic representation of our magnetometer which is an array of micro-SQUIDs. Its high sensitivity allows us to study single crystals of the order of 10 to 500 $\mu$m which are placed directly on the array.

I. INTRODUCTION

Magnetic molecular clusters are the final point in the series of smaller and smaller magnets from bulk matter to atoms. Up to now, they have been the most promising candidates to observe quantum phenomena since they have a well defined structure with well characterized spin ground state and magnetic anisotropy. These molecules are regularly assembled in large crystals where often all molecules have the same orientation. Hence, macroscopic measurements can give direct access to single molecule properties. The most prominent examples are a dodecanuclear mixed-valence manganese-oxo cluster with acetate ligands, Mn$_{12}$ acetate[3], and an octanuclear iron(III) oxo hydroxo cluster of formula [Fe$_8$O$_2$(OH)$_{12}$(tacn)$_6$]$^{8+}$, Fe$_8$[4], where tacn is a macrocyclic ligand. Both systems have a spin ground state of $S = 10$, and an Ising-type magneto-crystalline anisotropy, which stabilizes the spin states with $M = \pm 10$ and generates an energy barrier for the reversal of the magnetization of about 67 K for Mn$_{12}$ acetate and 25 K for Fe$_8$.

Fe$_8$ is particularly interesting because its magnetic relaxation time becomes temperature independent below 0.36 K showing for the first time that a pure tunneling mechanism between the only populated $M = \pm 10$ states is responsible for the relaxation of the magnetization[5]. Measurements of the tunnel splitting $\Delta$ as a function of a field applied in direction of the hard anisotropy axis showed oscillations of $\Delta$, i.e. oscillations of the tunnel rate[6]. In a semi-classical description[7], these oscillations are due to constructive or destructive interference of quantum spin phases of two tunnel paths[8]. Furthermore, parity effects were observed when comparing the transitions between different energy levels of the systems[9] which are analogous to the parity effect between systems with half integer or integer spins[1].

II. MICRO-SQUID TECHNIQUE

The technique of micro-SQUIDs is very similar to the traditional SQUID technique. The main difference is that the pick-up coil is replaced by a direct coupling of the sample with the SQUID loop (Fig. 1). When a small sample is directly placed on the wire of the SQUID loop, the sensitivity of the micro-SQUID technique is two orders of magnitude better than a traditional SQUID reaching $10^{-17}$ emu. This sensitivity is smaller when the sample is much bigger than the micro-SQUID.

Our new magnetometer is a chip with an array of micro-SQUIDs. The sample is placed on top of the chip so that some SQUIDs are directly under the sample, some SQUIDs are at the border of the sample and some SQUIDs are beside the sample (Fig. 2). When a SQUID is very close to the sample, it is sensing locally the magnetization reversal whereas when the SQUID is far, it is integrating over a bigger sample volume.

The high sensitivity of this magnetometer allows us to...
study single Fe₈ crystals of the order of 10 to 500 μm. The magnetometer works in the temperature range between 0.035 and 6 K and in fields up to 1.4 T with sweeping rates as high as 1 T/s, and a field stability better than a microtesla. The time resolution is about 1 ms allowing short-time measurements. The field can be applied in any direction of the micro-SQUID plane with a precision much better than 0.1° by separately driving three orthogonal coils. In order to ensure a good thermalisation, the crystal is fixed by using a mixture of araldite and silver powder.

![FIG. 2. Temperature (a) and field sweeping rate (b) dependence of hysteresis loops of Fe₈ molecular clusters.](image)

Resonant tunneling is evidenced by equally separated steps of ∆Hₑ ≈ 0.22 T which, at $T < 360$ mK, correspond to tunnel transitions from the state $M = -10$ to $M = 10 - n$, with $n = 0, 1, 2,...$. The resonance widths of about $0.05$ T are due to mainly dipolar fields between the molecular clusters.

Typical measurements of magnetic hysteresis curves for a crystal of molecular Fe₈ clusters are displayed in Fig. 2 and 3. The field was swept in direction of the easy axis of magnetization evidencing about equally separated steps at $Hₑ ≈ n \times 0.22$ T ($n = 1, 2, 3 ...$) which are due to a faster relaxation of magnetization at particular field values. The step heights (i.e. the relaxation rates) change when a constant transverse field is applied. It is the purpose of these article to present a detailed study of this behavior which is interpreted in terms of resonant tunneling between discrete energy levels of the spin Hamiltonian $S = 10$ of Fe₈.

![FIG. 3. Hysteresis loops measured in the presence of a constant transverse field, at 0.04 K. Insets: enlargement around the field $H = 0$. Notice that the sweeping rate is ten times slower for the measurements in the insets than that of the main figures.](image)

**III. LANDAU ZENER METHOD**

The simplest model describing the spin system of Fe₈ molecular clusters has the following Hamiltonian:

$$H = -DS^2_x + E (S^2_y - S^2_z) + gμ_B S H$$

($S_x, S_y,$ and $S_z$ are the three components of the spin operator, $D$ and $E$ are the anisotropy constants, and the last term of the Hamiltonian describes the Zeeman energy associated with an applied field $H$). This Hamiltonian defines a hard, medium, and easy axes of magnetization in $x$, $y$ and $z$ direction, respectively (Fig. 3). It has an energy level spectrum with $(2S + 1) = 21$ values which, in first approximation, can be labeled by the quantum numbers $M = -10, -9, \ldots, 10$. The energy spectrum, shown in Fig. 3, can be obtained by using standard diagonalisation techniques of the $[21 \times 21]$ matrix describing the spin Hamiltonian $S = 10$. In the low temperature limit ($T < 0.36$ K) only the two lowest energy levels with $M = \pm 10$ are occupied. The avoided level crossing around $H_z =$
0 is due to transverse terms containing $S_x$ or $S_y$ spin operators (see inset of Fig. 3). The spin $S$ is in resonance between two states when the local longitudinal field is close to the avoided level crossing ($< 10^{-8}$ T for the avoided level crossing around $H_z = 0$). The energy gap, the so-called tunnel splitting $\Delta$, can be tuned by an applied field in the $xy$-plane (Fig. 1) via the $S_z H_z$ and $S_y H_y$ Zeeman terms. It turns out that a field in $H_z$ direction (hard anisotropy direction) can periodically change the tunnel splitting $\Delta$. In a semi-classical description, these oscillations are due to constructive or destructive interference of quantum spin phases of two tunnel paths (Fig. 1). The period of oscillation is given by:

$$\Delta H = \frac{2k_B}{g\mu_B} \sqrt{2E(E + D)}$$  \hspace{1cm} (2)

The most direct way of measuring the tunnel splitting $\Delta$ is by using the Landau-Zener model which gives the tunneling probability $P$ when sweeping the longitudinal field $H_z$ at a constant rate over the avoided energy level crossing (see inset of Fig. 1):

$$P_{M, M'} = 1 - e^{-\frac{\pi a^2_1}{2\hbar g\mu_B |\Delta|} |dH/dt|}$$  \hspace{1cm} (3)

Here, $M$ and $M'$ are the quantum numbers of the avoided level crossing, $dH/dt$ is the constant field sweeping rates, $g \approx 2$, $\mu_B$ the Bohr magneton, and $\hbar$ Planck’s constant. In the following, we drop the index $M$ and $M'$. For very small tunneling probabilities $P$, we did multiple sweeps of the resonance transition. The relaxed magnetization after $N$ sweeps is given by ($n = 0$):

$$M(N) \sim \exp[-2PN] = \exp[-\Gamma t]$$  \hspace{1cm} (4)

where $N = \frac{\Delta H}{\hbar g\mu_B} t$ is the number of sweeps over the level crossing, $\Gamma = 2P_1 \frac{dH}{dt} = \frac{\Delta M}{M} \frac{dH}{dt}$ is the overall Landau-Zener transition rate, $\Delta M$ is the change of magnetization after one sweep, and $A$ is the amplitude of the ac-field. We have therefore a simple tool to obtain the tunnel splitting by measuring $P$, or $M(N)$ for $P << 1$.

In order to apply the Landau-Zener formula (Eq. 3), we first saturated the sample in a field of $H_z = -1.4$ T, yielding $M_\text{sat} = -M_s$. Then, we swept the applied field at a constant rate over one of the resonance transitions and measured the fraction of molecules which reversed their spin. This procedure yields the tunneling rate $P$ and thus the tunnel splitting $\Delta$ (Eq. 3). We first checked the predicted Landau-Zener sweeping field dependence of the tunneling rate. This can be done by plotting the relaxation of magnetization as a function of $t = N \frac{A}{dH/dt}$. The Landau-Zener model predicts that all measurements should fall on one line which was indeed the case for sweeping rates between 1 and 0.001 T/s (fig. 4). The deviations at lower sweeping rates, are mainly due to the ‘hole-digging mechanism’ which slows down the relaxation. In the ideal case, we should find an exponential curve (Eq. 3). However, this might be only the case in the long time regime (see inset of Fig. 4). The origin is not clear but it might be related to dipolar interactions and hyperfine couplings. For comparison, there is also a relaxation curve without ac-field at $H = 0$ which shows much slow relaxation.

FIG. 4. Unit sphere showing degenerate minima A and B which are joined by two tunnel paths (heavy lines). The hard, medium, and easy axes are taken in $x$, $y$ and $z$ direction, respectively. The transverse field $H_{\text{trans}}$ is applied in the $xy$ plane at an azimuth angle $\phi$. At zero applied field, the giant spin reversal results from the interference of two quantum spin paths of opposite direction in the easy anisotropy plane $yz$. By using Stokes theorem it has been shown that the path integrals can be converted in an area integral, giving that destructive interference, that is a quench of the tunneling rate, occurs whenever the shaded area is $k\pi/S$, where $k$ is an odd integer.

FIG. 5. Zeeman diagram of the 21 levels of the $S = 10$ manifold of Fe$_8$ as a function of the field applied along the easy axis. Form the bottom to the top, the levels are labeled with quantum numbers $M = \pm 10, \pm 9, ... 0$. The levels cross at fields given by $\mu_0 H_n \sim n 0.22$ T, with $n = 1, 2, 3, ...$. The inset displays the detail at a level crossing where the transverse terms (terms containing $S_x$ or/and $S_y$ spin operators) turn the crossing into an avoided crossing. The higher the gap $\Delta$, the stronger is the tunnel rate.
that the field sweeping rate is not too small because it works even in the presence of dipolar and hyperfine fields which spread the resonance transition provided that the field sweeping rate is not too small.

We also compared the tunneling rates found by the Landau-Zener method with those found using a square-root decay method which was proposed by Prokof’ev and Stamp, and found again a good agreement.

These measurements show that the Landau-Zener method is particularly adapted for molecular clusters because it works even in the presence of dipolar and hyperfine fields which spread the resonance transition provided that the field sweeping rate is not too small.

The corresponding tunnel splittings Δ oscillate with almost the same period of ca. 0.4 T (Fig. 5). In addition, comparing quantum transitions between $M = -S$ and $(S-n)$, with $n$ even or odd, revealed a parity (symmetry) effect which is analogous to the (Kramers) suppression of tunneling predicted for half integer spins. This behavior has been observed for $n = 0$ to 4. A similar strong dependence on the azimuth angle $\varphi$ was observed for all the resonances.

In the frame of the simple giant spin model (Eq. 1), the period of oscillation (Eq. 2) is $\Delta H = 0.26$ T for $D = 0.275$ K and $E = 0.046$ K as in Ref. 25. This is significantly smaller than the experimental value of ca. 0.4 T. In order to quantitatively reproduce the observed periodicity we have included forth order terms in the spin Hamiltonian (Eq. 1) as recently employed in the simulation of inelastic neutron scattering measurements and performed a diagonalization of the $[21 \times 21]$ matrix describing the $S = 10$ system. However, as the forth order terms are very small, only the term in $C(S^+_z + S^-_z)$, which is the most efficient in affecting the tunnel splitting $\Delta$, has been considered for the sake of simplicity. The calculated tunnel matrix elements for the states involved in the tunneling process at the resonances $n = 0, 1,$ and 2 are reported in Fig. 6, showing the oscillations as well as the parity effect for odd resonances. The period is reproduced by using $D = 0.292$ K $E = 0.046$ K as in Ref. 25 but with a different $C$ value of $-2.9 \times 10^{-5}$ K. The calculated tunneling splittings is however ca. 3 times smaller than the observed one. These small discrepancies are not surprising. In fact with the $C$ parameter we take into account the effects of the neglected higher order terms in $S_x$ and $S_y$ of the spin hamiltonian which, even if very small, can give an important contribution to the period of oscillation and dramatically affect $\Delta$, as first pointed out by Prokof’ev and Stamp. Our choice of the forth order terms suppress the oscillations of $\Delta$ for $|H_x| > 1.4$ T which could not be studied in the current set-up. Future measurements should focus on the higher field region in order to find a better effective Hamiltonian.

IV. OSCILLATIONS OF TUNNEL SPLITTING

Studies of the tunnel splitting $\Delta$, at the tunnel transition between $M = \pm 10$, as a function of transverse fields applied at different angles $\varphi$, defined as the azimuth angle between the anisotropy hard axis and the transverse field (Fig. 6) show that for small $\varphi$ angles the tunneling rate oscillates with a period between minima of ca. 0.41 T, whereas no oscillations showed up for large $\varphi$ angles (see Fig. 2A in Ref. 24). In the latter case, a much stronger increase of $\Delta$ with transverse field is observed. The transverse field dependence of the tunneling rate for different resonance conditions between the state $M = -10$ and $(S-n)$ can be observed by sweeping the longitudinal field around $H_z = n \times 0.22$ T with $n = 0, 1, 2, \ldots$ The corresponding tunnel splittings $\Delta$ oscillate with almost the same period of ca. 0.4 T (Fig. 5). In addition, comparing quantum transitions between $M = -S$ and $(S-n)$, with $n$ even or odd, revealed a parity (symmetry) effect which is analogous to the (Kramers) suppression of tunneling predicted for half integer spins. This behavior has been observed for $n = 0$ to 4. A similar strong dependence on the azimuth angle $\varphi$ was observed for all the resonances.

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FIG. 8. Measured tunnel splitting $\Delta$ as a function of transverse field for $\varphi \approx 0^\circ$, and for quantum transition between $M = -10$ and $(S - n)$. Note the parity effect which is analogous to the suppression of tunneling predicted for half integer spins. It should also be mentioned that internal dipolar and hyperfine fields hinder a quench of $\Delta$ which is predicted for an isolated spin.

FIG. 9. Calculated tunnel splitting $\Delta$ (Eq. 3) as a function of transverse field for quantum transition between $M = -10$ and $(10 - n)$ at $\varphi = 0^\circ$. Our choice of the forth order terms suppress the oscillations of $\Delta$ for $|H_x| > 1.4$ T. Future measurements should focus on higher transverse fields.

V. INTERMOLECULAR DIPOLE INTERACTION

Fig. 10 shows detailed measurement of the tunnel splitting $\Delta$ around a topological quench for the quantum transition between $M = -10$ and $(10 - n)$ at $\varphi = 0^\circ$. Note the strong dependence on the initial magnetization which demonstrates the dipolar interaction between Fe$_8$ molecular clusters.

VI. CONCLUSION

Our measurement technique is opening a way of directly measuring very small tunnel splittings of the order of $10^{-8}$ K not accessible by resonance techniques. We have found a very clear oscillation in the tunnel splittings $\Delta$, which are direct evidence of the role of the topological spin phase in the spin dynamics of these molecules. They are also the first observation, to our knowledge, of an "Aharonov-Bohm" type of oscillation in a magnetic system, analogous to the oscillations as a function of external flux in a SQUID ring. A great deal of information is contained in these oscillations, both about the form of the molecular spin Hamiltonian, and also about the dephasing effect of the environment. We expect that these oscillations should thus become a very useful tool for studying systems of quantum nanomagnets.

VII. ACKNOWLEDGMENT

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19. We supposed here that the forth and back sweeps give the same tunnel probability. This is a good approximation for $P << 1$ where next nearest neighbor effects can be neglected.
20. In order to avoid heating problems for measurements of $\Delta$ for $n > 1$, we started in a thermal annealed sample with $M_{in} = 0.95M_s$ instead of $M_{in} = -M_s$.
21. For small sweeping rates (depending on $\Delta$ at high sweeping rates), the mean internal field changes faster than the applied field leading to strong deviation from the Landau Zener model.
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