Nonadiabatic Landau-Zener tunneling in Fe₈ molecular nanomagnets

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Abstract. – The Landau-Zener method allows to measure very small tunnel splittings ∆ in molecular clusters Fe₈. The observed oscillations of ∆ 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. Studies of the temperature dependence of the Landau-Zener transition rate P gives access to the topological quantum interference between excited spin levels. The influence of nuclear spins is demonstrated by comparing P of the standard Fe₈ sample with two isotopically substituted samples. The need of a generalised Landau-Zener transition rate theory is shown.

During the last few decades, a large effort has been spent to understand the detailed dynamics of quantum systems that are exposed to time-dependent external fields and dissipative effects [1]. It has been shown that molecular magnets offer a unique opportunity to explore the quantum dynamics of a large but finite spin. These molecules are the final point in the series of smaller and smaller units from bulk magnets to single magnetic moments. They 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, Mn₁₂ [2], and an octanuclear iron(III) oxo-hydroxo cluster of formula [Fe₈O₂(OH)₁₂(tacn)₆]^{4+}, Fe₈ [3], where tacn is a macrocyclic ligand. Both systems have a spin ground state of S = 10, and an Ising-type magneto-crystalline anisotropy, which stabilises the spin states with the quantum numbers M = ±10 and generates an energy barrier for the reversal of the magnetisation of about 67 K for Mn₁₂ and 25 K for Fe₈ [2,3].

Fe₈ is particularly interesting for studies of quantum tunnelling because it shows a pure quantum regime, i.e. below 360 mK the relaxation is purely due to quantum tunnelling, and not to thermal activation [4]. We showed recently that the Landau-Zener method can be used to measure the very small tunnel splittings ∆ in Fe₈ [5]. The observed oscillations of ∆ 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 which was predicted by Garg [6]. This observation was the first direct evidence of the topological part of the quantum spin phase (Berry or Haldane phase [7,8]) in a magnetic system.

Recently, we demonstrated the influence of nuclear spins, proposed by Prokof’ev and Stamp [9], by comparing relaxation and hole digging measurements [10] of two isotopically substituted samples: i) the hyperfine coupling was increased by the substitution of $^{56}$Fe with $^{57}$Fe, and ii) it was decreased by the substitution of $^1$H with $^2$H. These measurements were supported quantitatively by numerical simulations taking into account the altered hyperfine coupling [10,11].

In this letter, we present studies of the temperature dependence of the Landau-Zener transition rate $P$ yielding a deeper insight into the spin dynamics of the Fe$_8$ cluster. By comparing the three isotopic samples, we confirm the influence of nuclear spins on the tunneling mechanism and in particular on the lifetime of the first excited states. Our measurements show the need of a generalised Landau-Zener transition rate theory taking into account environmental effects such as hyperfine and spin-phonon coupling [12].

All measurements of this article were performed using a new technique of micro-SQUIDs where the sample is directly coupled with an array of micro-SQUIDs [13]. The high sensitivity of this magnetometer allows us to study single Fe$_8$ crystals [14] of the order of 10 to 500 µm.

The crystals of the standard Fe$_8$ cluster, $^{57}$Fe$_8$ or Fe$_8$, [Fe$_8$(tacn)$_6$O$_2$(OH)$_{12}$]Br$_8$.9H$_2$O, where tacn = 1,4,7-triazacyclononane, were prepared as reported by Wieghardt et al. [14]. For the synthesis of the $^{57}$Fe-enriched sample, $^{57}$Fe$_8$, a 13 mg foil of 95% enriched $^{57}$Fe was dissolved in a few drops of HCl/HNO$_3$ (3 : 1) and the resulting solution was used as the iron source in the standard procedure. The $^2$H-enriched Fe$_8$ sample, $^{2}$H$_8$, was crystallised from pyridine-$d_5$ and D$_2$O (99%) under an inert atmosphere at 5°C by using a non-deuterated Fe(tacn)Cl$_3$ precursor. The amount of isotope exchange was not quantitatively evaluated, but it can be reasonably assumed that the H atoms of H$_2$O and of the bridging OH groups, as well as a part of those of the NH groups of the tacn ligands are replaced by deuterium while the aliphatic hydrogens are essentially not affected. The crystalline materials were carefully checked by elemental analysis and single-crystal X-ray diffraction.

The simplest model describing the spin system of Fe$_8$ molecular clusters has the following Hamiltonian [3]:

$$H = DS_z^2 + E(S_x^2 - S_y^2) + H_2 - g\mu_B\mu_0\vec{S}\cdot\vec{H}.\quad (1)$$

$S_x$, $S_y$, and $S_z$ are the three components of the spin operator, $D$ and $E$ are the anisotropy constants, $H_2$ takes into account weak higher-order terms [15,16], and the last term of the Hamiltonian describes the Zeeman energy associated with an applied field $\vec{H}$. This Hamiltonian defines a hard, a medium, and an easy axis of magnetisation in the $x$, $y$ and $z$ direction, respectively. It has an energy level spectrum with $(2S+1) = 21$ values which, in first approximation, can be labelled by the quantum numbers $M = -10, -9, ..., 10$. The energy spectrum can be obtained by using standard diagonalisation techniques of the [21×21] matrix describing the spin Hamiltonian $S = 10$. At $\vec{H} = 0$, the levels $M = \pm 10$ have the lowest energy. When a field $H_z$ is applied, the energy levels with $M \ll 0$ increase, while those with $M > 0$ decrease. Therefore, different energy values can cross at certain fields. This crossing can be avoided by transverse terms containing $S_x$ or $S_y$ spin operators which split the levels. The spin $S$ is in resonance between two states $M$ and $M'$ when the local longitudinal field is close to such an avoided energy level crossing ($|H_z| < 10^{-8}$ T for the avoided level crossing around $H_z = 0$). The energy gap, the so-called tunnel spitting $\Delta_{M,M'}$, can be tuned by an applied field in the $xy$-plane via the $S_zH_x$ and $S_yH_y$ Zeeman terms. It turns out that a field in the $H_x$ direction (hard anisotropy direction) can periodically change the tunnel splitting $\Delta$ as displayed in fig. 1,
Fig. 1 – Calculated tunnel splitting $\Delta_{M,M'}$ (eq. (1)) as a function of the transverse field $H_x$ for quantum transition between $M = \pm 10, \pm 9$ and $\pm 8$.

Fig. 2 – Field sweeping rate dependence of the tunnel splitting $\Delta_{-10,10}$ measured by a Landau-Zener method for three Fe$_8$ samples, for $H_x = 0$. The Landau-Zener method works in the region of high sweeping rates where $\Delta_{-10,10}$ is sweeping rate independent. Note that the differences of $\Delta_{-10,10}$ between the three samples are rather small in comparison to the oscillations in fig. 3.

where $H_2$ in eq. (1) was taken from [16]. In a semi-classical description, these oscillations are due to constructive or destructive interference of quantum spin phases of two tunnel paths [6].

A direct way of measuring the tunnel splittings $\Delta_{M,M'}$ is by using the Landau-Zener model [17,18] which gives the tunnelling probability $P_{M,M'}$ when sweeping the longitudinal field $H_z$ at a constant rate over an avoided energy level crossing [19]:

$$P_{M,M'} = 1 - \exp\left(-\frac{\pi \Delta_{M,M'}^2}{2\hbar g \mu_B |M - M'| \mu_0 dH_z/dt}\right).$$

Here, $M$ and $M'$ are the quantum numbers of the avoided energy level crossing, $dH_z/dt$ is the constant field sweeping rate, $g \approx 2$, $\mu_B$ the Bohr magneton, and $\hbar$ is Planck’s constant.

In order to apply the Landau-Zener formula (eq. (2)), we first cooled the sample from 5 K down to 0.04 K in a field of $H_z = -1.4$ T yielding a negative saturated magnetisation state. Then, we swept the applied field at a constant rate over the zero-field resonance transition and measured the fraction of molecules which reversed their spin. This procedure yields the tunnelling rate $P_{-10,10}$ and thus the tunnel splitting $\Delta_{-10,10}$ (eq. (2)). The predicted Landau-Zener sweeping field dependence of $P_{-10,10}$ can be checked by plotting $\Delta_{-10,10}$ as a function of the field sweeping rate which should show a constant, which was indeed the case for sweeping rates between 1 and 0.001 T/s (fig. 2). The deviations at lower sweeping rates are mainly due to the hole-digging mechanism [22,23] which slows down the relaxation. The comparison with the isotopically substituted Fe$_8$ samples shows a clear dependence of $\Delta_{-10,10}$ on the hyperfine coupling (fig. 2). Such an effect has been predicted for a constant applied field by Tupitsyn et al. [24].

All measurement so far were done in the pure quantum regime ($T < 0.36$ K) where transition via excited spin levels can be neglected. We discuss now the temperature region of small thermal activation ($T < 0.7$ K) where we should consider transition via excited spin levels [26]. We make the ansatz that only ground-state tunnelling ($M = \pm 10$) and transitions
viathefirstexcitedspinlevels\((M = \pm 9)\)arerelativefortemperaturesslightlyabove0.36 K.
We will see that this ansatz describes well our experimental data but, nevertheless, it would
be important to work out a complete theory [20].

In order to measure the temperature dependence of the transition rate, we used the
Landau-Zener method [17] as described above with a phenomenological modification of the
transitionrate\(P\) (foranegativesaturatedmagnetisation):

\[
P = n_{-10}P_{-10,10} + P_{\text{th}},
\]

where \(P_{-10,10}\) is given by eq. (2), \(n_{-10}\) is the Boltzmann population of the \(M = -10\) spin
level, and \(P_{\text{th}}\) is the overall transition rate via excited spin levels. \(n_{-10} \approx 1\) for the considered
temperature \(T < 0.7\) K and a negative saturated magnetisation of the sample.

Figure 3 displays the measured transition rate \(P\) for \(^{st}\)Fe\(_8\) as a function of a transverse
field \(H_x\) and for several temperatures. The oscillations of \(P\) are seen for all temperatures but
the periods of oscillations decreases for increasing temperature (fig. 4). This behaviour can be
explained by the giant spin model (eq. (1)) with higher-order transverse terms \((H_2)\). Indeed,
the tunnel splittings of excited spin levels oscillate as a function of \(H_x\) with decreasing periods
(fig. 1).

Figure 5 displays the transition rate via excited spin levels \(P_{\text{th}} = P - n_{-10}P_{-10,10}\). Surpris-
ingly, the periods of \(P_{\text{th}}\) are temperature independent in the region \(T < 0.7\) K. This suggests
that only transitions via excited levels \(M = \pm 9\) are important in this temperature regime.
This statement is confirmed by the following estimation [27], see also ref. [20].

Using eq. (2), typical field sweeping rates of 0.1 T/s, and tunnel splittings from fig. 1,
one easily finds that the Landau-Zener transition probability of excited levels is \(P_{-M, M} \approx 1\)
for \(M < 10\) and \(\overline{H} \approx 0\). This means that the relaxation rates via excited levels are mainly
governed by the lifetime of the excited levels and the time \(\tau_{\text{res}, M}\) during which these levels are
Fig. 5 – Transverse field dependence of $P_{th}$ which is the difference between the measured tunnel probability $P$ and the ground-state tunnel probability $n_{-10}P_{-10,10}$ measured at $T = 0.05$ K (see fig. 3). The field sweeping rate was 0.14 T/s. The long dotted lines indicate the minima of $P_{th}$, whereas the short dotted lines indicate the minima of $P_{-10,10}$.

Fig. 6 – Temperature dependences of $P_{th}$ for $H_x = 0$ for three Fe$_8$ samples. The field sweeping rate was 0.14 T/s. The dotted lines are fits of the data using eq. (5) [28].

in resonance. The latter can be estimated by

$$
\tau_{res,M} = \frac{\Delta_{-M,M}}{g \mu_B M \mu_0 d H_z / d t}.
$$

(4)

The probability for a spin to pass into the excited level $M$ can be estimated by $\tau^{-1}_M e^{-E_{10,M}/k_B T}$, where $E_{10,M}$ is the energy gap between the levels 10 and $M$, and $\tau_M$ is the lifetime of the excited level $M$. We obtain [27]

$$
P_{th} \approx \sum_{M=9,8} \frac{\tau_{res,M} e^{-E_{10,M}/k_B T}}{\tau_M} \approx \sum_{M=9,8} \frac{\Delta_{-M,M}}{\tau_M g \mu_B M \mu_0 d H_z / d t} e^{-E_{10,M}/k_B T}.
$$

(5)

Note that this estimation neglects higher excited levels with $|M| < 8$ [29]. Figure 6 displays the measured $P_{th}$ for the three isotopic Fe$_8$ samples. For 0.4 K $< T < 1$ K we fitted eq. (5) to the data leaving only the level lifetimes $\tau_9$ and $\tau_8$ as adjustable parameters. All other parameters are calculated using eq. (1) [28]. We obtain $\tau_9 = 1.0, 0.5, \text{ and } 0.3 \times 10^{-6}$ s, and $\tau_8 = 0.7, 0.5, \text{ and } 0.4 \times 10^{-7}$ s for $^{57}$Fe$_8$, $^{57}$Fe$_8$, and $^{57}$Fe$_8$, respectively. This result justifies our ansatz of considering only the first excited level for 0.4 K $< T < 0.7$ K. Indeed, the second term of the summation in eq. (5) is negligible in this temperature interval. It is interesting to note that this finding is in contrast to hysteresis loop measurements on Mn$_{12}$ [30] which suggested an abrupt transition between thermal assisted and pure quantum tunnelling [31]. Furthermore, our result shows clearly the influence of nuclear spins which seem to decrease the level lifetimes $\tau_M$, i.e. to increase dissipative effects.

The nuclear magnetic moment and not the mass of the nuclei seems to have the major effect on the dynamics of the magnetization. In fact the mass is increased in both isotopically modified samples, whereas the effect on the relaxation rate is opposite. On the other hand, ac susceptibility measurements at $T > 1.5$ K showed no clear difference between the three samples [32] suggesting that above this temperature, where the relaxation is predominantly
due to spin-phonon coupling [21,26], the role of the nuclear spins is less important. Although the increased mass of the isotopes changes the spin-phonon coupling, this effect seems to be small.

We can also exclude that the change of mass for the three isotopic samples has induced a significant change in the magnetic anisotropy of the clusters. In fact the measurements below $T < 0.35$ K, where spin-phonon coupling is negligible, have shown that i) the relative positions of the resonances as a function of the longitudinal field $H_z$ are unchanged [33], and ii) all three samples have the same period of oscillation of $\Delta$ as a function of the transverse field $H_x$ [5], a period which is very sensitive to any change of the anisotropy constants.

In conclusion, we presented detailed measurements based on the Landau-Zener method which demonstrated again that molecular magnets offer a unique opportunity to explore the quantum dynamics of a large but finite spin. We believe that a more sophisticated theory is needed which describes the dephasing effects of the environment.

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LEUENBERGER and LOSS [20] proposed recently that the incoherent Landau-Zener transition probability $P_{\text{inc}}$ has an exponent that is twice as large as the one of the coherent Landau-Zener transition probability $P_{\text{coh}}$. This is simply due to a different definition. Whereas $P_{\text{coh}}$ is defined as an escape probability, $1 - P_{\text{inc}}$ is defined as the difference of population of up and down spins. In all previous publications [5, 13], we did take into account this factor two when converting the measured change of magnetisation into an escape probability of incoherent Landau-Zener transitions (eq. (2)).

After distributing preprints of this work LEUENBERGER M. N. and LOSS D. worked out a theory considering only spin-phonon coupling, http://xxx.lanl.gov/cond-mat/9911065. They adjusted their result to our data and found spin-phonon coupling constants which are much larger than those found for Mn$_{12}$ [21]. See also ref. [12], Sec. 4.2 and the recent work of THORWART M., GRIFFONI M. and HÄNGGI P., http://xxx.lanl.gov/quant-ph/9912024 (1999).

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Using eq. (1) we found $\Delta_{-9,9}/k_B = 0.5 \times 10^{-5}$ K, $\Delta_{-8,8}/k_B = 0.2 \times 10^{-3}$ K, $E_{10,9}/k_B = 5.3$ K, and $E_{10,8}/k_B = 9.8$ K for $H = 0$.

Phonon-induced transitions with $|\Delta M| > 2$ are very small [26]. Also the Boltzmann factor $e^{-E_{10,8}/k_B T}$ is very small for $M < 8$ and $T < 1$ K.

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We observed a small shift of the resonances of the order of magnitude of 1 mT, positive for $^{57}$Fe and negative for $^{57}$Fe (M$_{\text{init}} = -M_s$). This can also be attributed to the modified hyperfine fields. However, a quantitative measurement is complicated by the fact that it is impossible to have two crystals with exactly the same shape, i.e. the same internal fields.