Single-molecule magnets (SMM) are considered the best systems for studying quantum tunneling of magnetization at the mesoscopic level. The first molecule shown to be a SMM was Mn$_{12}$ acetate [1]. It exhibits slow magnetization relaxation of its $S = 10$ ground state which is split by axial zero-field splitting. It was the first system to show thermally assisted tunneling of magnetization [2, 3, 4]. Fe$_8$ and Mn$_4$ SMMs were the first to exhibit ground state tunneling [5, 6]. Tunneling was also found in other SMMs (see, for instance, [7, 8, 9]). A detailed study of the influence of environmental degrees of freedom on the tunnel process has been started on Fe$_8$ and Mn$_{12}$ acetate (concerning phonons [10, 11], nuclear spins and dipolar couplings [12, 13, 14]) which were motivated by theories [15, 16, 17]. The spin-parity effect is among the fundamental predictions which have yet to be established at the mesoscopic level. It is predicted that quantum tunneling is suppressed at zero applied field if the total spin of the magnetic system is half-integer (Kramers degeneracy) but is allowed in integer spin systems. Van Hemmen and Sütò [18] were the first to suggest the absence of tunneling as a consequence of Kramers degeneracy [35]. It was then shown that tunneling can even be absent without Kramers degeneracy [19, 20, 21]. In this case, quantum phase interference can lead to destructive interference and thus suppress tunneling [21]. This effect was recently seen in Fe$_8$ and Mn$_{12}$ SMMs [22, 23].

There are several reasons why the first attempts [2, 24] to observe the spin-parity effect were unsuccessful. The main reason reflects the influence of environmental degrees of freedom that can induce or suppress tunneling: Firstly, hyperfine and dipolar couplings can induce tunneling via transverse field components; furthermore, intermolecular superexchange coupling may enhance or suppress tunneling depending on its strength; phonons can induce transitions via excited states; and finally, faster relaxing species can complicate the interpretation [13].

In this letter, we show that these problems can be overcome by studying the tunnel splitting as a function of transverse field. We selected three SMMs which revealed to be sufficiently small to show clearly ground state tunneling.

FIG. 1: Hysteresis loops of a single crystal of (a) Mn$_4$-(S=9/2) and (b) Mn$_4$-(S=8) molecular clusters at different temperatures and a constant field sweep rate $dH_z/dt = 0.07$ T/s.
The first is $[\text{Mn}_4\text{O}_3(\text{OSiMe}_3)(\text{OAc})_3(\text{dbm})_3]$, called Mn$_4$$-$(S = 9/2), with a half-integer ground state S = 9/2. The second is $[\text{Mn}_4(\text{O}_2\text{CMe})_2(\text{Hpdm})_6][\text{ClO}_4]_2$, called Mn$_4$$-$(S = 8), with an integer ground state S = 8. The third is the well known Fe$_8$ SMM with a S = 10 spin ground state. The preparation, X-ray structure, and detailed physical characterization of both Mn$_4$ molecules have been presented. The complex Mn$_4$$-$(S = 9/2) crystallizes in a hexagonal space group with a crystallographic C$_3v$ symmetry. The complex has a trigonal-pyramidal (highly distorted cubane-like) geometry. This complex is mixed-valent: Mn$^{III}$$^+$Mn$^{IV}$. The C$_3v$ axis passes through the Mn$^{IV}$ ion and the triply bridging siloxide group. DC and AC magnetic susceptibility measurements indicate a well isolated S = 9/2 ground state. The complex Mn$_4$$-$(S = 8) crystallizes in a triclinic lattice. The cation lies on an inversion center and consists of a planar Mn$_4$ rhombus that is also mixed-valent: Mn$^{II}$$^+$Mn$^{IV}$. DC and AC magnetic susceptibility measurements indicate a S = 8 ground state.

All measurements were performed using an array of micro-SQUIDs. The high sensitivity of this magnetometer allows us to study single crystals of SMMs of sizes of the order of 10 to 500 μm. The field can be applied in any direction by separately driving three orthogonal coils.

Before presenting our measurements we review briefly the giant spin model which is the simplest model describing the spin system of SMMs. The spin Hamiltonian is

$$H = -D S_z^2 + H_{\text{trans}} + g \mu_B \mu_0 \vec{S} \cdot \vec{H}$$

(1)

$S_x$, $S_y$, and $S_z$ are the three components of the spin operator; $D$ is the anisotropy constant defining an Ising type of anisotropy; $H_{\text{trans}}$, containing $S_x$ or $S_y$ spin operators, gives the transverse anisotropy which is small compared to $DS_z^2$ in SMMs; and the last term describes the Zeeman energy associated with an applied field $\vec{H}$. This Hamiltonian has an energy level spectrum with (2S + 1) values which, to a first approximation, can be labeled by the quantum numbers $m = -S, -(S-1), ..., S$ taking the z-axis as the quantization axis. The energy spectrum can be obtained by using standard diagonalization techniques. At $\vec{H} = 0$, the levels $m = \pm S$ have the lowest energy. When a field $H_z$ is applied, the levels with $m < 0$ increase in energy, while those with $m > 0$ decrease. Therefore, energy levels of positive and negative quantum numbers cross at certain values of $H_z$. It turns out that the levels cross at fields given by $\mu_0 H_z \approx n D/g \mu_B$, with $n = 0, 1, 2, 3, ...$.

When the spin Hamiltonian contains transverse terms ($H_{\text{trans}}$), the level crossings can be “avoided level crossings”. The spin $S$ is “in resonance” between two states when the local longitudinal field is close to an avoided level crossing. The energy gap, the so-called “tunnel splitting” $\Delta$, can be tuned by a transverse field (a field applied perpendicular to the $S_z$ direction) via the $S_z H_x$ and $S_y H_y$ Zeeman terms.

The effect of these avoided level crossings can be seen in hysteresis loop measurements. Figs. 1a and 1b show typical hysteresis loop measurements for single crystals of Mn$_4$$-$(S = 9/2) and Mn$_4$$-$(S = 8) (for Fe$_8$ data, see [12]). When the applied field is near an avoided level crossing, the magnetization relaxes faster, yielding steps separated by plateaus. As the temperature is lowered, there is a decrease in the transition rate due to reduced thermally assisted tunneling. A similar behavior was observed in Mn$_{12}$ acetate clusters. As seen for Fe$_8$ hysteresis loops become temperature-independent below 0.4 K indicating ground state tunneling. The field between two resonances allows us to estimate the anisotropy constants $D$. We obtain 0.68 K and 0.43 K for Mn$_4$$-$(S = 9/2) and Mn$_4$$-$(S = 8), respectively.

In order to establish the spin-parity effect, the tunnel splitting was measured as a function of transverse field. The field dependence of the tunnel splitting is expected to be very sensitively dependent on the spin-parity and the parity of the avoided level crossing. This approach is based on the Landau–Zener model that describes the nonadiabatic transition between the two states in a two-level system. The original work by Zener concentrated on the electronic states of a diatomic molecule, while Landau considered two atoms that undergo a scattering process. Their solution of the time-dependent Schrödinger equation of a two-level system can be applied to many physical systems and it has become an important tool for studying tunneling transitions. The Landau–Zener model has also been applied to spin tunneling in nanoparticles and clusters.

When sweeping the longitudinal field $H_z$ at a constant rate over an avoided energy level crossing, the tunneling...
probability \( P \) is given by

\[
P_{m,m'} = 1 - \exp\left[ -\frac{\pi \Delta^2_{m,m'}}{2\hbar g_{\mu_B} |m - m'| \mu_B dH_z / dt} \right]
\]  (2)

Here, \( m \) and \( m' \) are the quantum numbers of the avoided level crossing, \( dH_z / dt \) is the constant field sweep rate, \( g \approx 2 \), \( \mu_B \) is the Bohr magneton, and \( \hbar \) is Planck’s constant.

In order to apply quantitatively the Landau–Zener formula (Eq. 2), we first checked the predicted sweep field dependence of the tunneling rate. The SMM crystal was first placed in a high negative field to saturate the magnetization. Then, the applied field was swept at a constant rate over one of the resonance transitions and the fraction of molecules that reversed their spin was measured. The tunnel splitting \( \Delta \) was calculated using Eq. 2 and is plotted in Fig. 2 as a function of field sweep rate. The Landau–Zener method is applicable in the region of high sweep rates where \( \Delta \) is finite. However, depending on the spin-parity the sensitivity to an applied transverse field is completely different. The tunnel splitting increases gradually for an integer spin, whereas it increases rapidly for a half-integer spin. Note also that \( \Delta \) is plotted on a logarithmic scale in Fig. 3, and that the tunnel probability should depend on the second power of \( \Delta \) (Eq. 2). Therefore, our measurements show that the tunneling rate of a half-integer spin is strongly transverse field dependent, unlike the case for an integer spin SMM.

Figs. 4a and 4b present the first attempt to simulate the measured tunnel splittings for \( \text{Mn}_4 \) \( (S = 9/2) \). For simplicity, the calculated \( \Delta \) has been averaged over all possible orientation of the transverse field. (b) Same as in (a) but taking into account a Gaussian distribution of transverse field components with a half-width \( \sigma = 0.035 \) T.

Fig. 3 presents the measured tunnel splittings obtained by the Landau–Zener method as a function of transverse field.

FIG. 3: Tunnel splitting for three SMMs as a function of transverse field. The data for \( \text{Fe}_8 \) where taken from [33] with the transverse field applied along the medium hard axis.
tunneling. In our case, mainly hyperfine and dipolar couplings induce tunneling via transverse field components. Fig. 4b presents a simulation of the measured tunnel splitting when taking into account a Gaussian distribution of transverse field components with a width \( \sigma = 0.035 \text{ T} \). This value is in good agreement with other SMMs.

The simulation of measured tunnel splittings for \( \text{Mn}_4 \) \((S = 8)\) is much easier because an integer spin is not very sensitive to transverse field components resulting from hyperfine and dipolar couplings. We found that a second order term with \( E = 0.057 \text{ K} \) can describe well the data.

In conclusion, we have shown that the predicted spin parity effect \([18, 19, 20]\) can indeed be observed by measuring the tunnel splitting as a function of transverse field. An integer spin system is rather insensitive to small transverse fields whereas a half-integer spin systems is much more sensitive. However, a half-integer spin system will also undergo tunneling at zero external field as a result of environmental degrees of freedom such as hyperfine and dipolar couplings or small intermolecular superexchange interaction.

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