

Scaling of the susceptibility *vs.* magnetic-field sweep rate in Fe₈ molecular magnet

M. JORDI¹, A. HERNANDEZ-MÍNGUEZ¹, J. M. HERNANDEZ¹, J. TEJADA¹,
S. STROOBANTS², J. VANACKEN² and V. V. MOSHCHALOV²

¹ *Department de Física Fonamental, Universitat de Barcelona
Diagonal 647, 08024 Barcelona, Spain*

² *Pulsed Field Group, Laboratory of Solid-State Physics and Magnetism, K.U. Leuven
Celestijnenlaan 200D, B-3001 Leuven, Belgium*

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Abstract. – The dependence of the magnetization reversal on the sweep rate of the applied magnetic field has been studied for single crystals of Fe₈ magnetic molecules. Our experiments have been conducted at temperatures below 1 K and sweep rates of the magnetic field between 10³ T/s to 10⁴ T/s. The systematic shift of the values of the magnetic field at which the magnetization reversal occurs, indicates that this reversal process is not governed by the Landau-Zener transition model. Our data can be explained in terms of the superradiance emission model proposed by Chudnovsky and Garanin (*Phys. Rev. Lett.*, **89** (2002) 157201).

Introduction. – At zero magnetic field, the magnetic energy of high-spin molecular magnets has two symmetric minima with an energy barrier between them. The energy levels at both sides of this anisotropy barrier are separated by energies in the microwave range and show long lifetime. From the classical point of view, the magnetic relaxation in molecular magnets, like Mn₁₂ and Fe₈, can be seen as thermal activation over this barrier. However, when the thermal activation energy becomes small compared to the anisotropy energy, the relaxation is dominated by quantum tunneling through the barrier [1–3]. This mechanism has been successfully described in terms of single-molecule Landau-Zener transitions [4–8].

The spin Hamiltonian of the Fe₈ molecular magnet was deduced from electron paramagnetic resonance (EPR) experiments [9] and the occurrence of resonant tunneling in Fe₈ was detected by Sangregorio *et al.* from dc magnetization [3] and by Zhang *et al.* from ac susceptibility measurements [10]. In a first approximation the spin Hamiltonian of Fe₈ is given by

$$H = -DS_z^2 + ES_x^2 - g\mu_B \vec{H} \cdot \vec{S}, \quad (1)$$

where z and x denote the easy and hard axis, respectively. The values of $D = 0.229$ K and $E = 0.093$ K are known from EPR data [9]. Very similar values to these have been used, for

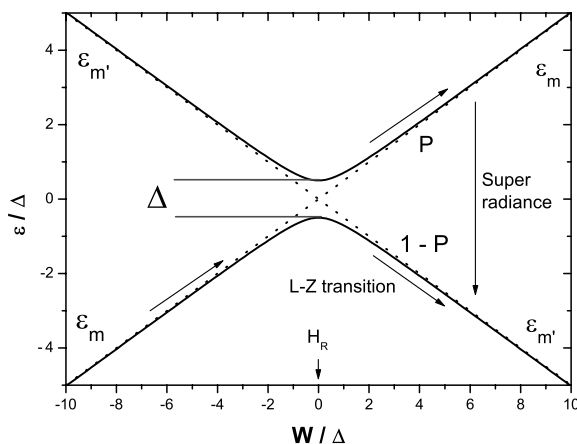


Fig. 1 – Plot of the energy of a pair of spin levels ε_m and $\varepsilon_{m'}$ *vs.* the energy bias $W = \varepsilon_m - \varepsilon_{m'} = g|m - m'|\mu_B(H(t) - H_R)$. H_R denotes the (second) resonance field. The total magnetization inversion occurs after crossing the resonance, at $H(t) > H_R$ via superradiant magnetic dipolar transitions between the levels m and m' , with unperturbed energies ε_m and $\varepsilon_{m'}$.

example, to explain the experimental results on the suppression of the spin tunneling rate due to the non-Kramers topological quenching of the tunneling [11], first suggested theoretically by Garg [12], and the quantum coherent oscillations of the spin [13]. Very recently, Chudnovsky and Garanin [14,15] have theoretically shown that molecular magnets and in particular Fe_8 can exhibit superradiance of both electromagnetic, as suggested by Dicke [16], and acoustic waves.

Experimental method. – The material studied by us is composed from Fe_8 micro single crystals synthesised according to the procedure published by Wiedghardt *et al.* [17]. X-ray diffraction was performed to confirm the single-phase structure. In the experiments we used a set of Fe_8 oriented microcrystals of 2 mm length and 0.6 mm diameter solidified in epoxy. The magnetization measurements below the blocking temperature and the ac susceptibility data of Fe_8 show that, for $H_z \neq nH_R$, the magnetization reversal occurs by thermal activation, whereas for $H_z = nH_R$ the reversal is due to quantum tunneling relaxation, as the magnetization response shows steps separated by $H_R = 0.24$ T. The measurements of the magnetization at high-field sweep rates at different temperatures below 1 K were carried out at the K. U. Leuven pulse facility [18,19], where the field sweep rate was varied between 10^3 and 10^4 T/s. The sample was submerged in liquid ^3He .

Results and discussion. – A very convenient way to determine experimentally the spin tunneling is based on sweeping the longitudinal field until making a pair of levels at the two sides of the barrier ε_m and $\varepsilon_{m'}$ to go through a resonance, see fig. 1. After crossing the resonance, the Landau-Zener probability for the spin of a single molecule to stay in the same well is given by [4–8]

$$P = \exp \left[- \frac{\pi \Delta_{m,m'}^2}{2\hbar v_m} \right], \quad (2)$$

where $\Delta_{m,m'}$ is the level splitting and v_m is the speed of the m level detuning, *i.e.* the energy sweep rate. The energy separation between the two levels is, therefore, $W = v_m t$. Moreover, it has been theoretically suggested [14] that in the case of fast-sweep experiments, the relaxation

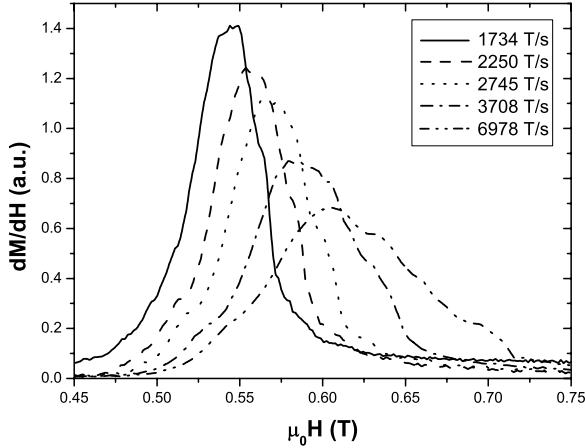


Fig. 2 – Plot of the dependence between dM/dH and H for different sweep rates at the second resonance.

process splits into two stages that are well separated from each other in time. The first stage is the well-known Landau-Zener process [4–8] appearing when the field is crossing a resonance and the second stage is the superradiant relaxation [13]. The Landau-Zener process begins immediately after the resonance is crossed and it ends effectively within a distance $\Delta_{m,m'}$ from the resonance. The superradiance emission process may take place after crossing the resonance if almost all molecules have not relaxed before by Landau-Zener process. As v_m increases, Landau-Zener probability P gets closer to 1 and the superradiance relaxation becomes more important. This is the case we discuss in this paper, see fig. 1, referred to fast-sweep experiments for which it is verified that

$$\varepsilon = \frac{\pi \Delta_{m,m'}^2}{2\hbar v_m} \ll 1$$

and then $P_{LZ} = \exp[-\varepsilon] \sim 1$. When the field is swept through the resonance at constant rate r , the relation between the energy sweep rate and the field sweep rate is $v_m = g|m - m'|\mu_B r$. At the superradiance stage it is also verified that emission must shift to higher fields at higher sweep rates, as we will see below.

In the fast-sweep rate experiments we determine experimentally the variation of magnetization with time, that is dM/dt , which may be converted into dM/dH as we know the sweep rate for the magnetic field. Our experimental procedure was the following: we first applied a positive magnetic-field pulse (pulse 1) that reached 5 T from 0 T, and then came back to 0 T. Immediately after, we applied a new pulse the same way as before (pulse 2). These two magnetization processes were followed by two identical negative-pulse variations from 0 T to -5 T and again to 0 T (pulse 3 and 4). The non-zero values for dM/dt do only appear in the case of pulses 1 and 3, as the pulses 2 and 4 were supposed to be applied to a saturated and aligned sample. Moreover, in the magnetization data from both pulses 1 and 3 we observe a single peak that appears exactly at the same absolute value of magnetic field, having the same intensity. In fig. 2, we show dM/dH vs. H for experiments performed at $T = 650$ mK and at different sweep rates when applying the first positive pulse (pulse 1). The maximum of these peaks is at a field value close to the second resonant field, $H_2 \sim 0.48$ T. We have controlled

the constancy of the temperature of the sample during all the magnetization processes by measuring the temperature of a RuO thermometer coupled to the sample, which is submerged in liquid helium.

The main result of these experiments is that the position of the dM/dH maximum shifts to higher fields at higher sweep rates, so that the spin inversion occurs at a field value higher than the resonance field. This is not consistent with the occurrence of tunneling by Landau-Zener process, but it may be explained by considering the theoretical suggestion of the relaxation via the emission of superradiance [15].

For experiments with a fast sweeping of the magnetic field, where it has been verified that $\varepsilon \approx \pi \Delta_{m,m'}^2 / 2\hbar v_m \ll 1$, the time derivative of $s_z = S_z/S$ can be written as

$$\frac{ds_z}{dt} = \frac{\alpha}{\hbar}(1 - s_z^2)W(t). \quad (3)$$

By considering that the field variation is linear with time, which is valid in our experiments close to the resonant field, eq. (3) can be rewritten as

$$\frac{ds_z}{dt} = \frac{\alpha}{\hbar}(1 - s_z^2)g|\Delta m|\mu_B r t = C(1 - s_z^2)rt \quad (4)$$

with

$$\alpha = \frac{1}{6}N\langle S_z \rangle^2 g^2 \left(\frac{e^2}{\hbar c} \right) \left(\frac{\Delta_{m,m'}}{m_e c^2} \right)^2, \quad (5)$$

where N is the total number of Fe_8 molecules in the sample, $S = 10$ is the spin of the molecule, g is the gyromagnetic ratio, e and m_e are the electron charge and mass, c is the speed of light, and $\langle S_z \rangle = (m' - m)/2$. Taking into account both the low value of the temperature of the experiment and the high sweep of the magnetic field, it is reasonable to assume that the dM/dH peaks observed for field values comprised between 0.5 T and 0.6 T correspond to ground-state tunneling at the second resonant field. That is, we are detecting the spin tunneling transitions between the states $m = -10$ and $m' = 8$.

By considering that $d(t\sqrt{r}) = \sqrt{r} dt$, and $H = rt$, eq. (4) can be written

$$\frac{r ds_z}{d(H\sqrt{r})} = C(1 - s_z^2)\sqrt{r}\frac{H}{r}. \quad (6)$$

Since $s_z \sim M$, we finally arrive at the superradiant constraint for the different parameters determining the experimental conditions, that are the magnetic field at superradiant emission, the relaxation of the magnetization and the value of the sweep rate at that point:

$$\frac{dM}{dH}\sqrt{r} \approx \frac{H}{\sqrt{r}}. \quad (7)$$

Using eq. (7) and the value of the resonant field obtained after fitting H as a function of \sqrt{r} , we were able to scale our experimental data, as shown in fig. 3. This allows us, using eq. (5), to estimate the constant $\alpha = 6 \cdot 10^{-7}$. For $N = 10^{18}$ molecules, which is the number of molecules in the sample, the value of $\Delta_{-10,8}$ results in 0.3 mK.

From the comparison between the theoretical value of $\Delta_{-10,8} \approx 6 \cdot 10^{-3}$ mK for the spin tunneling between states -10 and 8 , deduced from the spin Hamiltonian of eq. (1), and the value $\Delta_{-10,8} = 0.3$ mK determined from our experiments, it seems that we should consider the existence of a stronger transversal anisotropy. As in the case of the results obtained using Mn_{12} [19], we have to assume that the fast variation of the magnetic field may be responsible

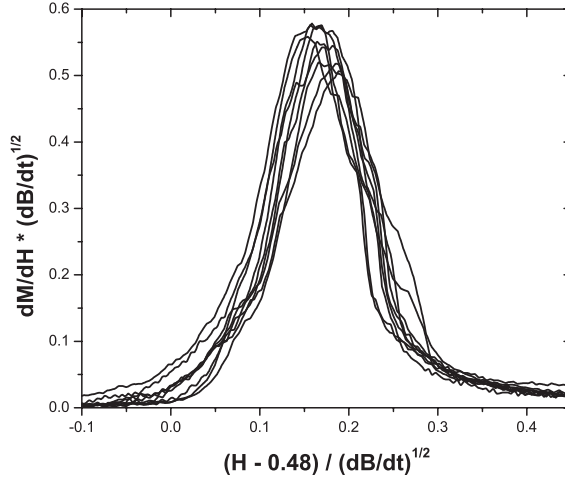


Fig. 3 – Plot of $\sqrt{r}(dM_z/d\delta H)$ vs. $\delta H/\sqrt{r}$, where $dB/dt \equiv r$ and $\delta H = H(t) - H_R$ at the second resonance, $\mu_0 H_R = 0.48$ T, for all curves at different sweep rates.

for modifying the transversal-anisotropy term. As the tunnel splitting of the resonant levels appears in the $[(m' - m)/2]$ -th order of the perturbation theory on E , then $\Delta_{-10,8} \propto (E/D)^9$. This clearly indicates that a small modification of the E value produces dramatic changes in the tunneling rate. In fact, by changing E from the value of 0.093 K, determined by EPR and used in many experiments [9, 11, 13, 20], to the new value $E' = 0.145$ K, we recover the tunneling splitting found from our experiments.

The absence of self-heating in our experiments has been proven by performing two different set of experiments. In the first set, we have observed that, at constant sweep rate of $6 \cdot 10^3$ T/s, the position of the peak of dM/dH does not shift when changing the temperature between 0.6 and 1 K. In the second type of experiments we studied the position of the peak for different shots at constant temperature $T = 550$ mK, and we observed that the maximum of dM/dH does not shift when we apply a single shot (that is, the pulse goes from zero to a field of about 5 T and back to zero) or an oscillating shot in which the pulse is not damped, but oscillates from negative field back to positive field and so on. The time between two consecutive cycles is about 4 ms which is a very small value for the sample to recover its initial temperature in case of being heated. Moreover, the emission of phonons or photons does not require the heating of the sample as they are a consequence of the evolution of the decay of a huge number of molecules living in the excited state after crossing the resonance. As a consequence of the different wavelength of phonons and photons, the number of molecules involved in the case of the emission of photons should be much larger than that in case of phonons. The size of our crystals allows both effects.

Summary. – In conclusion, we have found that Fe_8 exhibits a spin relaxation effect at high-field sweep rates, which seems to be in good agreement with the theory of collective electromagnetic relaxation. This relaxation effect is analogous to that reported for Mn_{12} -acetate, suggesting that this is a general phenomenon. Anyway, the unambiguous proof for the superradiance will be the detection of the electromagnetic radiation emitted by the molecular magnets.

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REFERENCES

- [1] FRIEDMAN J., SARACHIK M., TEJADA J. and ZIOLO R., *Phys. Rev. Lett.*, **76** (1996) 3830.
- [2] HERNÁNDEZ J. M., ZHANG X. X., LUIS F., BARTOLOMÉ J., TEJADA J. and ZIOLO R., *Europhys. Lett.*, **35** (1996) 301.
- [3] SANGREGORIO S., OHM T., PAULSEN C., SESSOLI R. and GATTESCHI D., *Phys. Rev. Lett.*, **78** (1997) 4645.
- [4] LANDAU L. D., *Phys. Z. Sowjetun.*, **2** (1932) 46; ZENER C., *Proc. R. Soc. London, Ser. A*, **137** (1932) 696.
- [5] DOBROVITSKY V. V. and ZVEZDIN A. K., *Europhys. Lett.*, **38** (1997) 377.
- [6] GUNTHER L., *Europhys. Lett.*, **39** (1997) 1.
- [7] LEUENBERGER M. N. and LOSS D., *Phys. Rev. B*, **61** (2000) 12200.
- [8] CHUDNOVSKY E. M. and GARANIN D. A., *Phys. Rev. Lett.*, **87** (2001) 187203; GARANIN D. A. and CHUDNOVSKY E. M., *Phys. Rev. B*, **65** (2002) 094423.
- [9] BARRA A. L., DEBRUNNER P., GATTESCHI D., SCHULZ CH. E. and SESSOLI R., *Europhys. Lett.*, **35** (1996) 133.
- [10] ZHANG X. X., HERNANDEZ J. M., DEL BARCO E., TEJADA J., ROIG A., MOLINS E. and WIEGHARDT K., *J. Appl. Phys.*, **85** (1999) 5633.
- [11] WERNSDORFER W. and SESSOLI R., *Science*, **284** (1999) 133.
- [12] GARG A., *Europhys. Lett.*, **22** (1993) 205.
- [13] DEL BARCO E., VERNIER N., HERNÁNDEZ J. M., TEJADA J., CHUDNOVSKY E. M., MOLINS E. and BELLESA G., *Europhys. Lett.*, **47** (1999) 722.
- [14] CHUDNOVSKY E. M. and GARANIN D., *Phys. Rev. Lett.*, **89** (2002) 157201.
- [15] CHUDNOVSKY E. M. and GARANIN D., cond-mat/0406383-v1.
- [16] DICKE R. H., *Phys. Rev.*, **93** (1954) 99.
- [17] WIEDGHARDT K., POHL K., JIBRIL I. and HUTTNER G., *Angew. Chem. Int. Ed. Engl.*, **23** (1997) 4645.
- [18] VANACKEN J., *Physica B*, **294** (2001) 591.
- [19] VANACKEN J., STROOBANTS S., MALFAIT M., MOSHCHALOV V. V., JORDI M., TEJADA J., AMIGO R., CHUDNOVSKY E. M. and GARANIN D. A., cond-mat/0404041-v1.
- [20] DEL BARCO E., HERNÁNDEZ J. M., TEJADA J., BISKUP N., ACHEY R., RUTEL I., DALAL N. and BROOKS J., *Phys. Rev. B*, **62** (2000) 3018.