Nuclear spin driven resonant tunnelling of magnetisation in Mn$_{12}$ acetate

W. Wernsdorfer$^1$, R. Sessoli$^2$ and D. Gatteschi$^2$

$^1$ Lab. de Mag. Louis Néel – CNRS, BP166, 38042 Grenoble, France
$^2$ Dept. of Chemistry, Univ. of Florence, Via Maraglino 77, 50144 Firenze, Italy

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Abstract. – Current theories still fail to give a satisfactory explanation of the observed quantum phenomena in the relaxation of the magnetisation of the molecular cluster Mn$_{12}$ acetate. In the very low temperature regime, Prokof’ev and Stamp recently proposed that slowly changing dipolar fields and rapidly fluctuating hyperfine fields play a major role in the tunnelling process. By means of a faster relaxing minor species of Mn$_{12}$ac and a new experimental ‘hole digging’ method, we measured the intrinsic line width broadening due to local fluctuating fields, and found strong evidence for the influence of nuclear spins on resonance tunnelling at very low temperatures (0.04 – 0.3 K). At higher temperature (1.5 – 4 K), we observed a homogeneous line width broadening of the resonance transitions being in agreement with a recent calculation of Leuenberger and Loss.

Observation of mesoscopic quantum phenomena in magnetism has remained a challenging problem. The first striking demonstration of quantum tunneling and quantum phase interference was found on Mn$_{12}$ acetate and Fe$_8$, molecular clusters having a spin ground state $S = 10$ [1, 2, 3, 4]. Several models and theories have been proposed to explain in detail the experimental results, published during the last five years by several authors [5], but there is not yet satisfactory agreement between theory and experiments concerning mainly the relaxation rate and the resonance line width [5]. This letter is intended to report more accurate measurements which should help to find a satisfactory explanation of the observed quantum phenomena.

Several authors have pointed out that in the Mn$_{12}$ carboxylate family different isomeric forms give rise to different relaxation rates [5]. This has also been observed in Mn$_{12}$ acetate [2]. We found that a minor species Mn$_{12}$ac(2) [2], randomly distributed in the crystal of the major species Mn$_{12}$ac(1), exhibits a faster relaxation rate which becomes temperature independent below 0.3 K. Even if this second species has been only partially characterised [2] we can exploit it as a local probe providing unique information on the tunnelling process. We used a recently developed method [10, 11] for measuring the intrinsic line width broadening...
due to local fluctuating fields and found strong evidence for the influence of nuclear spins on resonance tunnelling.

In the first part of this letter, we focus on the low temperature and low field limit which is particularly interesting because phonon-mediated relaxation is astronomically long and can therefore be neglected. In this limit, only the two lowest levels with quantum numbers \( M_z = \pm 10 \) are involved. They are coupled by a tunnel matrix element \( \Delta/2 \) where \( \Delta \) is the tunnel splitting which is estimated to be about \( 10^{-10} \) K for Mn\(_{12}\) [12]. In an ideal system, resonant tunnelling requires that the magnetic field (local to the giant spin) is smaller than the field associated with the tunnel splitting \( \Delta \) which means a field smaller than \( 10^{-9} \) T for the Mn\(_{12}\)ac clusters. This fact would make it very difficult to observe the tunnelling of isolated giant spins at constant applied field. This dilemma is solved by invoking the dynamics of dipolar interaction between molecules and nuclear spins [12]. The tunnelling scenario can be summarised as follows: the rapidly fluctuating hyperfine field brings molecules into resonance. The dipolar field of tunnelled spins can lift the degeneracy and remove from resonance a large number of neighbouring spins. However, a gradual adjustment of the dipolar fields across the sample (up to 0.03 T in Mn\(_{12}\)ac), caused by tunnelling relaxation, brings other molecules into resonance and allows continuous relaxation. Therefore, one expects a fast relaxation at short times, and slow logarithmic relaxation at long times.

Recently, we developed a method [10, 11] for measuring the intrinsic line width broadening due to local fluctuating fields of the nuclear spins. It is based on the general idea that the short time relaxation rate is directly connected to the number of molecules which are in resonance at a given longitudinal applied field \( H \). The Prokof'ev - Stamp theory [12] predicts that the magnetisation should relax at short times with a square-root time dependence:

\[
M(H, t) = M_{in} + (M_{eq}(H) - M_{in}) \sqrt{\Gamma_{\text{sqrt}}(H) t} \tag{1}
\]

Here \( M_{in} \) is the initial magnetisation at time \( t = 0 \) (i.e. after a rapid field change), and \( M_{eq}(H) \) is the equilibrium magnetisation. The rate function \( \Gamma_{\text{sqrt}}(H) \) is proportional to the normalised distribution \( P(H) \) of molecules which are in resonance at the applied field \( H \):
Fig. 2. – Typical relaxation measurements of the minor species Mn$_{12}$ac(2) [9] measured at H = 0.39 T and for several temperatures. For each curve, the major species Mn$_{12}$ac(1) was demagnetised [13] and Mn$_{12}$ac(2) was saturated in a field of -1.4 T. The $\Gamma_{\text{sqrt}}$ relaxation rate was approximately found in the range from 0.014 > $M/M_S$ > 0.01, i.e. in the short time region. $M_S$ is the magnetisation of saturation of the whole crystal.

$$
\Gamma_{\text{sqrt}}(H) \sim \frac{\Delta^2}{\hbar} P(H)
$$

where $\hbar$ is Planck’s constant. Thus, the measurements of $\Gamma_{\text{sqrt}}(H)$, as a function of $H$, should give direct access to the distribution $P(H)$. Our measuring procedure is as follows. Starting from a well defined magnetisation state [13], we apply a magnetic field $H$ in order to measure the short-time square root relaxation behaviour. By using eq. (1), we get the rate function $\Gamma_{\text{sqrt}}(H)$ at the field $H$. Then, starting again from the same well defined magnetisation state, we measure $\Gamma_{\text{sqrt}}(H)$ at another field $H$, yielding the field dependence of $\Gamma_{\text{sqrt}}(H)$ which is proportional to the dipolar distribution $P(H)$ (eq. (2)).

This technique can be used for following the time evolution of molecular states in the sample during a tunnelling relaxation [1]. Starting from a well defined magnetisation state [3], and after applying a field $H_{\text{dig}}$, we let the sample relax for a time $t_{\text{dig}}$, called ‘digging field and digging time’, respectively. During the digging time, a small fraction of the molecular spins tunnel and reverse the direction of their magnetisation. Finally, we apply a field $H$ to measure the short time relaxation in order to get $\Gamma_{\text{sqrt}}(H)$ (eq. (1)). The entire procedure is then repeated to probe the distribution at other fields $H$ yielding $\Gamma_{\text{sqrt}}(H, H_{\text{dig}}, t_{\text{dig}})$ which is proportional to the number of spins which are still free for tunnelling. With this procedure one obtains the distribution $P(H, H_{\text{dig}}, t_{\text{dig}})$, which we call the ‘tunnelling distribution’.

We used this new technique, which we call ‘hole digging’ method [14], for studying Fe$_8$ molecular clusters [1] and found that tunnelling causes rapid transitions of molecules near $H_{\text{dig}}$, thereby “digging a hole” in $P(H, H_{\text{dig}}, t_{\text{dig}})$ around $H_{\text{dig}}$, and also pushing other molecules away from resonance. The hole widens and moves with time, in a way depending on sample shape; the width dramatically depends on thermal annealing of the magnetisation of the sample. For small initial magnetisation [13], the hole width shows an intrinsic broadening which may be due to nuclear spins [11].

For Mn$_{12}$ac(1) [9], $T < 1.5$K and small applied fields, relaxation measurements are very time consuming because the pure quantum relaxation rate between $M_x = \pm 10$ is of the order of years or longer [13]. However, we found that one can use the minor species Mn$_{12}$ac(2) [9]
which showed to have a much faster tunnelling rate. Furthermore, it has the advantage of being diluted over the entire crystals with a concentration of 1 to 2 percent, thus the internal dipolar fields hardly change during relaxation of Mn$_{12}$ac(2). As Mn$_{12}$ac(2) experiences the same environment (concerning mainly hyperfine fields) as the major species Mn$_{12}$ac(1), we propose to use Mn$_{12}$ac(2) as a local probe of any fluctuating field acting on the giant spins of Mn$_{12}$ac molecular clusters.

Below about 1.5 K, we found that the magnetisation of Mn$_{12}$ac(2) can be reversed in an applied field smaller than 2 T whereas that of Mn$_{12}$ac(1) hardly reverses because of the very small tunnelling rate. Fig. 1 presents a typical hysteresis loop measurements of Mn$_{12}$ac(2) which is almost temperature independent below 0.6 K [16]. These loops are strongly field sweeping rate dependent and show quantum tunnelling resonances at about equidistant fields of ∆H ≈ 0.39 T in comparison to 0.45 T for Mn$_{12}$ac(1).

Fig. 2 presents typical relaxation measurements of the minor species Mn$_{12}$ac(2). For each curve, the major species Mn$_{12}$ac(1) was demagnetised [13] and Mn$_{12}$ac(2) was saturated in a field of -1.4 T. Approximate square root relaxation was found in the range from 0.014 > M/M$_S$ > 0.01, where M$_S$ is the magnetisation of saturation of the entire crystal. The fact that the relaxation is not exactly proportional to $\sqrt{t}$ in the short time region, is irrelevant for the discussion of this letter [17].

Fig. 3a presents tunnelling distributions for Mn$_{12}$ac(2) for digging times between $t_0 = 0$
Fig. 4. – Hole line width $\sigma$, obtained by the measurements of quantum hole digging like in Fig. 3 (a) and (b), as a function of digging time for several temperatures. The intrinsic line width $\sigma_0$ is obtained by an linear extrapolation to $t_{\text{dig}} = 0$ s.

and 128 s. Note the depletion ("hole digging") around the digging field $H_{\text{dig}} = 0.39$ T. This hole-digging arises because only spins in resonance can tunnel. Although the hole is narrow, it is still several orders of magnitude larger than the field associated with the tunnel splitting $\Delta$.

The hole could be fitted to a Gaussian function yielding the line width $\sigma$ (see Fig. 3b) which we studied as a function of temperature and digging time (fig. 4). We defined an intrinsic line width $\sigma_0$ by a linear extrapolation of the curves to $t_{\text{dig}} = 0$. For temperatures between 0.04 and 0.3K, $\sigma_0 \approx 12$ mT. For $T > 0.3$ K, $\sigma_0$ increase rapidly.

The physical origin of the line width $\sigma_0$ is tentatively assigned to the fluctuating hyperfine fields. A simple calculation of the random hyperfine field distribution was made by Hartmann-Boutron et al. [18], who evaluated the maximum nuclear field operating on the lowest $M = 10$ levels of Mn$_{12}$. Using the same approach it is possible to calculate the whole spectrum of hyperfine levels. Assuming for the hyperfine coupling constants the values $a$(MnIII)$= 6.9$ mT and $a$(MnIV)$= 8.5$ mT, in agreement with currently accepted values for these ions [19], we calculate a Gaussian distribution of fields with a width of ca. 16 mT, in good agreement with the above reported experimental result. A detailed calculation of the random hyperfine field distribution can be found in Ref. [12].

We applied also the 'hole digging' method at temperatures between 1.5 and 4 K. At these temperatures, the relaxation rates of the minor species are very fast and can therefore be neglected. As pointed out by several groups, the relaxation of the major species Mn$_{12}$ac(1) is non-exponential at temperatures below 4 K but, nevertheless, we approximately adjusted an exponential law for the short time relaxation regime ($1 - 100$ s) in order to yield a relaxation rate $\Gamma$. We emphasise that the Prokof’ev Stamp theory [12] cannot be applied in the higher temperature regime because it neglects thermal activation to higher energy levels. However, the main idea of the ‘hole digging’ method should still hold, i.e. it should answer the question of whether the line width is homogeneously or inhomogeneously broadened. A typical result of the ‘hole digging’ experiment at 2 K is presented in Fig. 5 which shows that it is impossible to dig a hole in the $\Gamma(H)$ dependence suggesting that the line width is homogeneously broadened, as first suggested by Friedman et al. [6]. This finding is also in good agreement with a recent calculation of Leuenberger and Loss [20], see also [21] which is based on thermally assisted spin tunnelling induced by quadratic anisotropy and weak transverse magnetic fields. Their model is minimal in the sense that it is sufficient to explain the measurements without including hyperfine fields. Indeed, our measurements show that the inhomogeneous hyperfine broadening
of about 12 mT is small compared to the homogeneous broadening of about 30 mT (see fig. 5) which might be due to spin-phonon coupling [22].

In conclusion, this letter is intended to report more accurate measurements which should help to find a satisfactory explanation of the observed quantum phenomena in molecular clusters. We used the recently developed 'hole digging' method for measuring the intrinsic line width broadening due to local fluctuating fields and found strong evidence for the influence of nuclear spins in the tunnel process at low temperature. At higher temperatures, spin-phonon coupling seems to dominate the resonant quantum tunnel transitions which leads to homogeneously broadened line widths.

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This reasoning supposes that the inhomogeneous hyperfine broadening of about 12 mT is temperature independent in the region between 0.04 and 3 K.

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[2] The minor species of Mn$_{12}$ acetate are present in all currently synthesised crystals. Since it has first been mentioned by Sessoli et al. [1], several authors realised the presence of these minor species but they have never been studied in detail. Our main results of a detailed study, which will be published elsewhere [BARRA A.L. et al., to be published], are resumed as follows: Currently available Mn$_{12}$ acetate crystals contain 5 to 8 % of minor species which in our hypothesis correspond to defective sites in the crystal lattices showing modification of the coordination octahedron of a manganese(III) for the formation of hydrogen bonds with the disordered carboxylic acid molecules of solvation. We call Mn$_{12}$ac(1) the major species, Mn$_{12}$ac(2) the minor species in the bulk of the crystals. While the anisotropy easy axis of Mn$_{12}$ac(1) is aligned with the crystallographic axis, we found four easy axis of Mn$_{12}$ac(2) related by the four-fold symmetry axis of the tetragonal space group and forming an angle of 10° with the c-axis. The tilting of the anisotropy easy axis is due to the breaking of the tetragonal symmetry of the Mn$_{12}$ac molecule. The anisotropy barrier of Mn$_{12}$ac(2) is reduced to about 45 K (as determined through ac-measurements [NOVAK M. et al., to be published] and EPR [BARRA A.L. et al., to be published] in comparison to 65 K for Mn$_{12}$ac(1). We found that Mn$_{12}$ac(2) is dispersed in a diluted way over the whole crystal and not forming domains as suggested in ref. [TAKEDA K., AWAGA K. and INABE T., Phys. Rev. B., 57 (1998) R11062]. The SQUID array magnetometer allowed also to evidence other fast relaxing species mainly located at the surface of the crystal with no particular orientation of the easy axis.
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[6] We achieved a well define magnetisation state by different methods: (i) cooling the sample from 5 K to 40 mK in an applied field of H = 0 or -1.4 T, yielding the demagnetised or saturated magnetisation state of the entire crystal, respectively; (ii) first cooling the sample from 5 K to 40 mK in H = 0, then applying a field of H = -1.4 T for about 10 s, yielding a state where the major species Mn$_{12}$ac(1) is completely demagnetised whereas the minor species Mn$_{12}$ac(2) is saturated; (iii) one can also quench the sample from 5 K to 40 mK in a small field of few 10 – 2 T. When the quench is fast (few seconds), the sample’s magnetisation does not have time to relax, either by thermal or quantum transitions. This procedure yields a frozen thermal equilibrium distribution.
[7] The ‘hole digging’ method is in analogy to the ‘hole burning’ method, currently used in high density optical storage [HASAN Z., et al., Applied Physics Letters, 72 (1998) 2373] and single molecule spectroscopy [Xie X. S. and Trautman J. K., Annual Review of Physical Chemistry, 49 (1998) 441]. The main difference is due to the fact that the hole is not only due to depleting of molecules in resonance at $H_{dig}$ but also to shifting other molecules away from resonance due to the dipolar coupling.
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[9] For these measurements, we used an array of micro-SQUID with a very high sensitivity. We could investigate singles crystals 10 to 100 µm in size. The magnetometer is working in the temperature range between 35 mK and 6 K. Field sweeping rates can be as high as 1 T/s with a maximum field of 1.4 T. The time resolution is about 1 ms allowing short-time measurements.
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