Experimental evidence of the dependence of spin tunnelling on the concentration of dislocations in Mn$_{12}$ crystals

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Abstract. – We present experimental results on resonant spin tunnelling in a single crystal of Mn$_{12}$-2Cl benzoate with different concentration of dislocations. The time evolution of the magnetisation follows the stretched exponential, $M(t) \propto \exp\left[-(t/\tau)^\beta\right]$ over a few time decades. The values of $\tau$ and $\beta$ deduced from experiment have been used to determine the concentration of dislocations before and after the cooling-annealing process, using the algorithm recently suggested by Garanin and Chudnovsky.

The crystals of molecular clusters are soft and fragile. They must contain a large number of dislocations which rearrange atoms in their immediate vicinity. Dislocations are formed by the frozen in lattice disorder when crystallization takes place. In the case of molecular clusters, the dislocations can also be introduced by performing thermal cycles which produce dilations and compressions of the lattice. Many techniques are now available for the study of dislocations. The two most important techniques are X-ray diffraction and transmission electron microscopy.

After five years of experiments [1, 2, 3, 4, 5, 6] and theoretical studies [7, 8, 9, 10, 11] a new theoretical approach [12] has been suggested which may fully explain the mechanism of thermally assisted resonant tunnelling in crystals of Mn$_{12}$ molecular clusters. Chudnovsky and Garanin have theoretically shown [13, 14] that spin tunnelling in Mn$_{12}$ clusters must be dominated by dislocations. Some of the theoretical suggestions of Chudnovsky and Garanin have been recently confirmed in experiments [14, 15, 16]. In this paper we report results of our study of the effect of crystal defects on the tunnelling process. For this purpose, we have compared the results of quantum magnetic relaxation experiments on a single crystal of Mn$_{12}$-2Cl benzoate (Mn$_{12}$Cl) before and after suffering thermal shocks.

At low temperature the intramolecular exchange interactions render an effective spin $S=10$ for this molecular cluster. The Mn$_{12}$Cl crystallizes in an orthorhombic structure, $a = 2.275$

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nm, \( b = 1.803 \ \text{nm} \) and \( c = 1.732 \ \text{nm} \) with two molecules per unit cell \([17, 18]\). The magnetic core and the local symmetry of each molecule are identical to the case of Mn\(_{12}\)Ac. However, in contrast to Mn\(_{12}\)Ac, the magnetic easy axes of Mn\(_{12}\)Cl molecules lie alternatively on the direction (011) or (01T), being nearly perpendicular to their nearest neighbors. A fresh single crystal of Mn\(_{12}\)Cl clusters was first characterized by X-ray diffraction. Then we performed low temperature magnetic relaxation experiments. After this we cycled the temperature of the crystal between 80 K and 300 K by introducing it alternatively in liquid nitrogen during five minutes and in water during five minutes. This cooling-annealing process was repeated four times after which the crystal was again characterized by both X-ray diffraction and magnetic characterization measurements. A second cooling-annealing treatment, followed by X-ray and magnetic characterization measurements, was also performed. Our idea is to combine the thermal treatments with the defects induced during the X-ray characterization to increase the number of dislocations.

The crystal was mounted on the top of a glass capillary, glued at the prism base with its long dimension, (012) direction, oriented along the capillary. The crystal was kept on the capillary along all the performed thermal shocks, diffraction and magnetisation experiments.

The thermal shocks generate a large temperature gradient in the crystal producing radial and tangential tensions that favor the propagation of dislocations across the crystal, probably starting at point defects frozen during the growing of the crystal. The extension of these dislocations by the whole crystal converts the initial single crystal in a multidomain crystal being each element of it slightly misaligned with respect to its neighbors. This is what is known as a mosaic crystal and it is well known that as the crystals contain more and more dislocations greater is the mosaicity. The amount of misalignment is related with the widening of the Bragg peaks along the \( \omega \) \([24, 25, 26]\) axis and in the case of our single crystal after the thermal shocks, is of some tenths of a degree. Due to this low value, the crystal is still considered as a single crystal but with a larger mosaicity. The shape and size of a Bragg peak, except for instrumental parameters, depend on the shape and size of the crystal, on the spectral composition of the X-ray beam and on the mosaicity of the crystal. It is also known that the lack of monochromaticity elongates the peak along the \( \omega - 2\theta \) direction \([19, 20, 21]\). This effect together with mosaicity widening leads to an idealized hexagonally shaped diffraction peak. In our experiments low angle peaks were selected in order to reduce the monochromaticity effect.

After a random searching of diffraction peaks at \( \theta \) angles larger than 10\(^\circ\), the spots were indexed to check their single crystal origin, the crystal orientation and to get their cell parameters by using a four-circle single-crystal X-ray diffractometer (Enraf-Nonius CAD4, MoKa radiation). The reflections \( (\pm 2, \pm 2, \pm 2) \) were selected as they were low angle and intense. After centering, bi-dimensional profiles of these peaks were recorded at constant steps on \( \omega \) and \( \theta \). The same profiles were also measured after the thermal treatment. See the two peaks on Figure 1.

Although a precise analysis of diffraction spots shape is complicated, it is easier in the current case as we are comparing the same reflections on the same crystals, we can attribute all the changes to variations of mosaicity. All the measured reflections showed a widening of the peaks along the \( \omega \) direction after the thermal treatment, while keeping similar widths in the \( \theta \) direction. One of those reflections has been arbitrarily selected and depicted in Figure 1. The \( \omega \) widening even overcomes the predefined scan width, as can be clearly seen in the Figure 1. A flattening of the peaks occurs, reducing their maximum intensity by a factor of about 3 due to the \( \omega \) spreading out. In Table I appear the values of the \( \omega \) widths, \( \Delta \omega \), obtained by fitting the peaks of Figure 1 to a 2D lorentzian function. It is clear that \( \Delta \omega \) increases with the heat treatments. Assuming that the concentration of dislocations is proportional the
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ω-widening, it may be concluded that the number of dislocations existing in the Mn$_{12}$ single crystal has increased by near an order of magnitude with the thermal processes.

The energy barrier that separates the spin states $m > 0$ and $m < 0$ in Mn$_{12}$ molecular clusters derives from the Hamiltonian

$$\mathcal{H} = -AS_z^2 - BS_z^4 + C(S_z^4 + S_z^4) + \mathcal{H}_{dip} + \mathcal{H}_{hf},$$

where $A = 0.38(1) cm^{-1}$ and $B = 8.2(2) \times 10^{-4} cm^{-1}$ and $C = 3 \times 10^{-5} cm^{-1}$ [19, 20, 21]. The first two terms of the spin Hamiltonian generate spin levels $S_z$ inside each well and the $C$ term corresponds to the fourth order anisotropy term which contains spin operators that do not commute with $S_z$ causing, therefore, tunnelling. $\mathcal{H}_{dip}$ and $\mathcal{H}_{hf}$ are due to magnetic dipole fields and hyperfine interactions, respectively, which also cause tunnelling. When an external field is applied along the easy axis of the molecules producing the crossing of energy levels, the shortcut between degenerate $m$ and $-m$ levels, at the resonant fields, has been interpreted as due to the tunneling. In the presence of tunnelling, the activation energy is, therefore, at the $m$ tunnelling level instead of that at the top of the energy barrier. But with only these terms in the Hamiltonian it is not possible to get a fully quantitatively explanation for all the experimental facts. Very recently, Chudnovsky and Garanin [12, 13] have suggested the existence of a new term in the Hamiltonian, $\mathcal{H}_{me} = E(S_z^2 - S_0^2)$, which is due to the magnetoelastic coupling and mostly causes the spin tunnelling in the Mn$_{12}$ clusters. That is, this second order anisotropy term which is prohibited in a perfect crystal of Mn$_{12}$, is always present in real crystals due to the lattice distortions associated with the presence of dislocations.

Table I – ω-widths of the (222) reflection peaks obtained by fitting them to the 2D lorentzian

| H.T.   | $\Delta \omega \times 10^{-3}$ degree |
|--------|-------------------------------------|
| Before | 222 ± 6                             |
| After 1st | 479 ± 12                           |
| After 2nd | 1470 ± 60                          |
The magnetic relaxation experiments were performed as follows: the single crystal is cooled in the presence of a 3 T field from above the blocking temperature and at the desired lower temperature the magnetic field is switched off. The variation of the magnetisation with time, $M(t)$, is then recorded. Figure shows $M(t)$ before and after the second cooling - annealing process at three different temperatures. These curves have been fitted, within the entire time interval, by a stretched exponential function $M(t) \propto \exp\left[-(t/\tau)^\beta\right]$. In Table II, we list the values for $\tau$ and $\beta$ deduced from the fitting procedure. We have found that the values of both $\tau$ and $\beta$ decrease when increasing the concentration of dislocations. Both $\tau$ and $\beta$ have been found to decrease when lowering the temperature of the relaxation experiment.

The question now is to use, if it is possible, the variation of the values of $\tau$ and $\beta$ to get a quantitative estimation of the variation of the density of dislocations with the thermal process. That is, the curves of Figure 2 correspond to the magnetisation relaxation associated with the tunnelling events contributing to the resonance at zero field and are very sensitive to the concentration of dislocations. The reason for that lies in the fact that the value of the transverse anisotropy causing tunnelling for each molecule is very much dependent on the

Table II – Parameters obtained from the fitting of the relaxation data to a stretched exponential function for different temperatures and heat treatments.

| $T$ (K) | H.T.    | $\tau$ (s) | $\beta$ |
|---------|---------|------------|---------|
| 2.2     | Before  | $69 \times 10^3$ | 0.54    |
|         | After 1st | $57 \times 10^3$ | 0.51    |
|         | After 2nd | $10 \times 10^3$ | 0.43    |
| 2.4     | Before  | $46 \times 10^2$ | 0.59    |
|         | After 1st | $39 \times 10^2$ | 0.53    |
|         | After 2nd | $10 \times 10^2$ | 0.46    |
| 2.6     | Before  | 690         | 0.66    |
|         | After 1st | 700         | 0.65    |
|         | After 2nd | 240         | 0.54    |
location of the molecule with respect to the dislocation. As Chudnovsky and Garanin have demonstrated, the tunnelling probability of different spin levels overlap for different molecules. That is, the tunnelling magnetisation at each time is associated with the broad spectrum of molecules located at different distances from the core of a dislocation.

A few observations are in order before discussing the model we propose to explain our data:

a) The molecules close to the nucleus of dislocations are those relaxing faster and their number increases with the density of dislocations, b) As the temperature of the relaxation experiment increases, more and more molecules located far away from the dislocations contribute to the relaxation, c) Only in the absence of dislocations the relaxation should be pure exponential, d) due to dislocations there is a distribution of transversal anisotropy $E$ values associated with different locations of molecules with respect to the core of a dislocation. This distribution, $f(E, c)$, may be well represented by a Gaussian which center and width depend on the concentration of dislocations, $c$. The fact that the tunnelling rate depends strongly on $E$ values suggest that there is a distribution of transition probabilities.

That is, the amount of relaxing magnetisation at each time is written as

$$M(t) \propto \int_0^\infty e^{-\Gamma(E,T)t} f(E, c) dE$$

(2)

where $\Gamma(E,T)$ is the effective rate of relaxation for those clusters with perpendicular anisotropy $E$. In order to compute this parameter we have used the expression given by Friedman

$$\Gamma(E) = \Gamma_0 \exp(-E_0/T) + \sum_{m=1}^{10} \frac{\Gamma_0}{1 + \frac{E_m}{\Delta m}} \exp(-E_m/T)$$

(3)

where

$$\Delta_m = \frac{2D}{\sqrt{(2m-2)!!}} \frac{(S+m)!}{(S-m)!} \left(\frac{E}{2D}\right)^m$$

(4)

is the tunnelling splitting for the level $m$, $\Gamma_0$ is the attempt frequency, $T$ is the temperature, and $E_m$ is the energy of level $m$. Although the analysis of Chudnovsky and Garanin was performed for the uniaxial crystal of Mn$_{12}$-Acetate, the above formulas are rather general and can be equally applied to Mn$_{12}$Cl crystals.

Solving equation (2) we have seen that for a wide range of $T$ and $c$ values, the resulting magnetic relaxation follows very well the stretched exponential function. By direct comparison of the values of the parameters $\tau$ and $\beta$ deduced theoretically with those obtained from the experiment, we have estimated the concentration of dislocations of the crystal before and after the heat treatments. The results are summarized in Table III and show clearly that the concentration of dislocations increases with the heat treatments.

Assuming that the $\omega$-width, shown in Table I, is proportional to the concentration of dislocations, the ratio $\Delta\omega/c$ should be a constant. In Table III, we present the values of this ratio for the different thermal treatments. It can be seen that the ratio $\Delta\omega/c$ remain constant with the heat treatments.

This expression allows us to consider the transition probabilities through each level, fact that must be introduced to explain the thermally assisted nature of the resonant tunnelling phenomena observed in the kelvin regime.
In conclusion, combining the results of X-ray diffraction and magnetic relaxation we have show quantitatively that the tunneling probability increases when introducing dislocations in the matrix.

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