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Experimental evidence of the dependence of spin tunneling on the concentration of dislocations in Mn_{12} crystals

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Abstract

We present experimental results on the influence of the concentration of dislocations on resonant spin tunneling in a thermally treated single crystal of Mn_{12}-2Cl benzoate. The time evolution of the magnetization follows a stretched exponential law over a few time decades for all concentrations. The experimental values for the parameters entering this law were used to derive the thermal-dependent concentration of dislocations. We propose a new scaling term to account for the thermally assisted resonant tunneling at finite temperatures.

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Keywords: Quantum tunneling; Molecular magnet; Magnetic relaxation; Dislocation

In the last few years, high spin molecular clusters have acquired a great importance because of their use for testing quantum phenomena, like tunneling or computing. In this respect, the relaxation of the magnetic moment plays a crucial role and has generated many controversy because of the number of physical mechanisms that can be involved. If all the Mn_{12} molecules were affected by the same crystal field, the relaxation would be purely exponential. But in the kelvin regime, the relaxation deviates from this behavior and becomes clearly nonexponential in the subkelvin range [1,2]. Dipolar and hyperfine fields, which are usually invoked to originate the transversal field needed for tunneling [3–5], cannot account for this behavior. A new approach by Chudnovsky and Garanin (CG) [6,7] suggests that dislocations (defects in the crystal structure) may fully explain the mechanism of thermally assisted resonant tunneling in crystals of Mn_{12} molecular clusters. In this model, the molecules near dislocations evolve faster towards the equilibrium than the furthest.

The spin Hamiltonian relevant for our purposes is

$$H = -DS_z^2 - H_z S_z + H_{\mathrm{me}}, \qquad (1)$$

where x, y and z are, respectively the hard, middle and easy anisotropy axes of the crystal, $D = 0.65$ K is the longitudinal anisotropy, $\mathbf{S}$ is the spin operator ($S = 10$), $\mathbf{H}$ is the longitudinal magnetic field, $H_{\mathrm{me}} = E(S_x^2 - S_y^2)$ is the magnetoelastic coupling, which is considered as the main source of spin tunneling in the Mn_{12} clusters, and E is the transversal anisotropy.

In order to check this model, we analyzed the results of low-temperature magnetic relaxation experiments in a fresh single crystal of Mn_{12}-2Cl benzoate (Mn_{12}Cl) submitted to a cooling–annealing (CA) treatment. The crystal was cooled in a 3 T field from above the blocking temperature (3.2 K) down to a target temperature, at which the magnetic field was switched off, and the variation of the magnetization with time was then recorded. After this, the crystal was alternatively immersed, for periods of 5 min, in liquid nitrogen and water to cycle its temperature between 80 and 300 K. This process was repeated four times, and the whole CA treatment was carried twice. X-ray diffraction and

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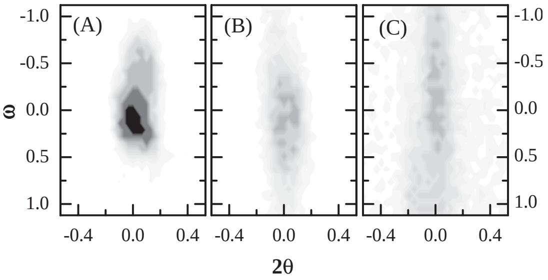

Fig. 1. ω–θ plot of the $(\underline{2}\,2\,2)$ reflection of the $Mn_{12}Cl$ crystal before (A) and after one (B) and two (C) CA treatments.

Table 1
Concentration of dislocations, c, ω-width of the X-ray diffraction plots, $\Delta\omega$, and $\Delta\omega/c$ ratio for the two CA treatments

CA treatments	c (10^{-4})	$\Delta\omega$ (10^{-3} degree)	$\Delta\omega/c$
0	3.0 ± 0.5	222.0 ± 6.0	740 ± 140
1	6.0 ± 1.0	479.0 ± 12.0	700 ± 150
2	20.0 ± 4.0	1470.0 ± 60.0	740 ± 180

magnetic relaxation measurements were performed before and after every CA treatment.

The thermal shocks generate a large temperature gradient in the crystal that produces radial and tangential tensions that favor the propagation of dislocations across the crystal, probably starting at point defects frozen during the growing process. The growth of the concentration of dislocations was extensively discussed in our previous work [8]. Fig. 1 show the ω–θ plot of X-ray diffraction data, in which the broadening of the peak in the ω direction caused by the CA treatments can be clearly observed. The ω-widths, $\Delta\omega$, obtained by fitting these peaks to a 2D Lorentzian are summarized in Table 1.

Due to the dislocations, there is a distribution of E values, $f(E,c)$, well represented by a Gaussian whose center and width depend on the concentration of dislocations, c. The amount of relaxing magnetization at each time is written therefore as

$$M(t) \propto \int_0^\infty e^{-\Gamma(E,T)t} f(E,c)\,dE, \tag{2}$$

where $\Gamma(E,T)$ is an effective rate of relaxation [6,7]. Solving this equation in a wide range of T and c values, the resulting magnetic relaxation follows very well a stretched exponential function, $\exp[-(t/\tau)^\beta]$. By direct comparison of the values of the parameters τ and β derived theoretically with those obtained by fitting the experimental relaxation curves to the same function, we estimated the concentration of dislocations of the crystal before and after the two CA treatments. The results are summarized in Table 1 and show clearly that the concentration of dislocations increases with the treatments. Assuming that the ω-width of the X-ray plot is proportional to the concentration of dislocations, the ratio $\Delta\omega/c$ should be independent of the number of CA treatments, as Table 1 reflects with a less-than-6% error.

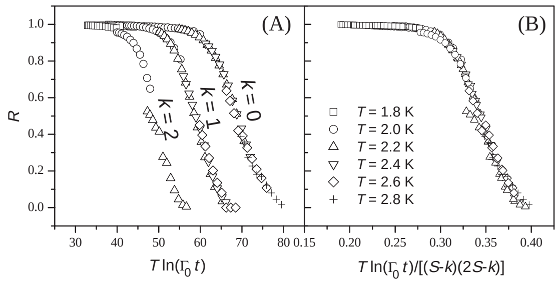

Fig. 2. $T\ln t$ plot of the amount of magnetic relaxation R (A), and universal scaling law for all temperatures and resonances (B).

In order to obtain another proof of the influence of the dislocations on the relaxation process, we used the Landau–Zener method [9,10]. After the second CA treatment, we measured the magnetization before, M_i, and after, M_f, a field variation, ΔH, around a tunneling resonance (labelled k), for different field sweeping rates, a. The amount of relaxing magnetization, $R \equiv (M_f - M_{eq})/(M_i - M_{eq})$, is proportional to $\exp(-\Gamma t)$, where M_{eq} is the equilibrium magnetization, $t \equiv \Delta H/a$ is the experimental time, and Γ is related to the effective energy barrier that separates the ground and tunneling states, U, via the Arrhenius law, $\Gamma = \Gamma_0 \exp(-U/k_BT)$. Due to the wide distribution of E, we should use a broad range of a values to measure the whole relaxation process, which is a very difficult task with our experimental system. Instead we measured at different temperatures to promote the fast relaxation of the molecules furthest from the dislocations. Fig. 2A shows a $T\ln t$ plot of R for different tunneling resonances ($k = 0, 1, 2$). Introducing an extra term $(S-k)$ into the CG model, to account for the thermally assisted resonant tunneling at any finite temperature, we found that all curves in Fig. 2A collapse into one universal scaling law for all temperatures and resonances, $T\ln(\Gamma_0 t)/[(S-k)(2S-k)]$ (Fig. 2B).

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