

## Quantum tunnelling in molecular magnets by a novel type of frequency-domain magnetic spectroscopy

The Department of Physics, University of Stuttgart, Germany, has investigated spin relaxation in the molecular magnet  $Mn_{12}$  using novel high frequency magnetic spectroscopy. The team is interested in understanding the phenomena of macroscopic quantum effects and how these systems might serve as a new approach in, for example, magnetic data storage, spin electronics, and quantum computers.

In the last decade, molecular chemistry has had a large impact in the field of nanoscale magnetism by providing molecular magnets - large molecules or clusters with magnetic properties. Magnetic hysteresis, however, is purely molecular in origin. These systems have been dubbed "single molecule magnets". These clusters are crystalline materials, where all the magnetic objects are well defined – with the same shape, size, and orientation.

Molecular magnetic clusters have small spins compared to usual fine magnetic particles and quantum effects are more likely to be revealed in these systems. They are unique objects with which to study interesting physical phenomena on the mesoscopic scale. Molecular magnets exhibit novel properties, such as molecular magnetic bistability, macroscopic quantum tunnelling of magnetisation, quantum phase interference, quantum coherence, and giant magnetostriction.

The team have studied spin relaxation in the prototype molecular magnet,  $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]_2CH_3COOH \cdot 4H_2O$ , abbreviated  $Mn_{12}ac$  or simply  $Mn_{12}$  (Figure 1). Due to strong anisotropy, the magnetic moment freezes along one of the two easy directions at low

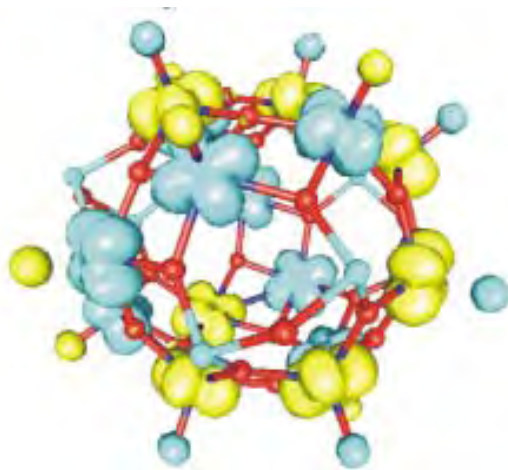


Figure 1: Structure of  $Mn_{12}$ . The eight  $Mn^{3+}$  and four  $Mn^{4+}$  lead to a total spin  $S=10$  of the molecule. Due to the molecular anisotropy, the magnetisation is directed either up or down.

temperatures. This is governed by a crystal field which splits the ground  $S = 10$  multiplet and provides a quasidoublet structure  $|\pm m\rangle$  of the lowest energy levels. The energy barrier  $\Delta E \sim 60$  K between the two lowest lying states  $|\pm 10\rangle$  determines the thermally activated relaxation of the magnetisation in  $Mn_{12}$ .

Using a new type of frequency-swept EPR the team measured the transmission of light through the sample using very long wavelength light (approx 1 mm). The sample is positioned in a specially modified Oxford Instruments Spectromag 4000. It has very large windows (more than 5 cm outer windows and about 2 cm at the variable temperature insert (VTI), which are made of Mylar-VM). The study involves absorption (due to magnetic losses) as a function of frequency (40-1400 GHz,  $1-45\text{ cm}^{-1}$ ) at different temperatures (1.5 - 300 K), different magnetic fields ( $<8$  T), and different orientations of the field and the radiation. This new technique, frequency domain magnetic spectroscopy (FDMS), could be used to resolve a large number of problems in chemistry, physics and material sciences.

In a low-energy optical set up the magnetic absorption of  $Mn_{12}$  is recorded as a function of frequency in a constant

magnetic field. Very sharp and pronounced absorption lines can be observed due to the crystal field transitions within the  $S=10$  ground multiplet. The lines shift in the presence of an external magnetic field and this enables study of the Gaussian and asymmetric line shape of  $Mn_{12}$  single crystals.

In order to study relaxation phenomena, the team magnetically polarise the system in a strong field at high temperature before cooling it down. By reversing the external magnetic field, the intensities of the  $|\pm 10\rangle \rightarrow |\pm 9\rangle$  transitions redistribute. Below  $T = 2$  K resonant quantum tunnelling is directly observed as "tunnel dip" in the

absorption spectra of polycrystals (Figure 2). The team quantitatively describe its observations by taking into account inhomogeneous line broadening, the time dependence of the level population during the relaxation process, and the resonance behaviour of the relaxation rate due to quantum tunnelling near the avoided level crossing.

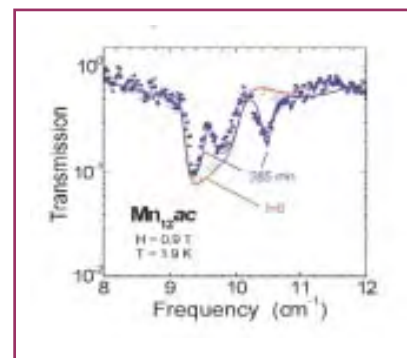


Figure 2 Transmission of electromagnetic radiation through a polycrystalline  $Mn_{12}$  pellet at  $T = 1.9\text{K}$ . After the direction of the magnetic field has been inverted, a broad absorption line is observed around  $9.5\text{cm}^{-1}$ . Due to tunneling of the spins a narrow dip occurs in this absorption band (tunnel dip). The spins relax faster and show up on the other side of the energy barrier as seen by the sharp line at  $10.5\text{cm}^{-1}$ .

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