Quantum Tunneling of Magnetization in a Large Molecular Nanomagnet – Approaching the Mesoscale

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A Mn30 molecular cluster is established to be the largest single-molecule magnet (SMM) discovered to date. Magnetization versus field measurements show coercive fields of about 0.5 T at low temperatures. Magnetization decay experiments reveal an Arrhenius behavior and temperature-independent relaxation below 0.2 K diagnostic of quantum tunneling of magnetization through the anisotropy barrier. The quantum hole digging method is used to establish resonant quantum tunneling. These results demonstrate that large molecular nanomagnets, having a volume of 15 nm³, with dimensions approaching the mesoscale can still exhibit the quantum physics of the microscale.

The study of the interface between classical and quantum physics has always been a fascinating area, but its importance has nevertheless grown dramatically with the current explosive thrusts in nanoscience. Taking devices to the limit of miniaturization (the mesoscale and beyond) where quantum effects become important makes it essential to understand the interplay between the classical properties of the macroscale and the quantum properties of the microscale. This is particularly true in nanomagnetism, where many potential applications require monodisperse, magnetic nanoparticles. One source of such species are single-molecule magnets (SMMs) individual molecules that function as single-domain magnetic particles. Below their blocking temperature, they exhibit magnetization hysteresis, the classical macroscopic property of a magnet, as well as quantum tunneling of magnetization (QTM) and quantum phase interference and quantum superposition of states for quantum computing. QTM is advantageous for some potential applications of SMMs, e.g. in providing the quantum superposition of states for quantum computing, but it is a disadvantage in others such as information storage where it would lead to loss of preferential spin alignment. Large SMMs approaching the mesoscale have long been the target of synthesis, and an important question for these (and other mesoscale magnetic particles) is whether they might still unequivocally demonstrate quantum properties, as theoretically predicted.

In this letter, we show that a Mn30 molecular cluster is by far the largest SMM to date, and show that it unambiguously still exhibits QTM. This establishes that the quantum physics of the microscale can also be observed in large molecular nanomagnets.

The Mn30 molecular cluster has the formula [Mn30O24(OH)8(O2CCH2CMMe3)32(H2O)2(MeNO2)4].xCH2Cl2·0.5H2O and crystallizes in the monoclinic space group C2/c with each Mn30 on a crystallographic C2 rotation axis. The molecules are thus all parallel with their molecular C2 axes (z axes) aligned along the crystal b axis. Each Mn30 comprises a Mn/O magnetic core and quantum superposition of states for quantum computing, but it is a disadvantage in others such as information storage where it would lead to loss of preferential spin alignment. Large SMMs approaching the mesoscale have long been the target of synthesis, and an important question for these (and other mesoscale magnetic particles) is whether they might still unequivocally demonstrate quantum properties, as theoretically predicted.

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The data were fit by diagonalization of the spin Hamiltonian matrix assuming only the ground state is populated and incorporating axial anisotropy (DSz²) and Zeeman terms, and employing a full powder average; the Mn30 is thus modelled as a giant spin with Ising-like anisotropy. The corresponding Hamiltonian is given by equation (1):

\[ \mathcal{H} = -D S_z^2 + \mathcal{H}_{\text{trans}} + g \mu_B \mu_0 \vec{S} \cdot \vec{H} \]  

(1)

where D is the axial anisotropy constant, Sz is the z-component of the spin operator S, \( \mathcal{H}_{\text{trans}} \) is the transverse anisotropy containing Sz and Sz operators, g is the electronic g-factor, \( \mu_0 \) is the Bohr magneton, \( \mu_0 \) is the vacuum permeability, and \( \vec{H} \) is the applied field. The last term in eq. 1 is the Zeeman energy associated with an applied field. The fit parameters were S = 5, D = -0.73 K, and g = 2.00, with the transverse anisotropy \( \mathcal{H}_{\text{trans}} \) not included for simplicity (in fact, inclusion of a small transverse anisotropy term involving the transverse
FIG. 1: Schematic view of the Mn/O magnetic core of a Mn$_4$, Mn$_{12}$, and Mn$_{30}$ SMMs. The Mn atoms are depicted larger than the O atoms.

anisotropy constant, $E$, had no significant effect on the fit). These values suggest an upper limit to the potential energy barrier $U$ to magnetization relaxation (reversal) of $U = S^2|D| = 18$ K, a value potentially large enough to make Mn$_{30}$ a SMM at sufficiently low temperatures. This was therefore explored by hysteresis loop, relaxation, and hole digging measurements.

Studies were performed on single crystals using an array of micro-SQUIDs [19]. Hysteresis in magnetization versus magnetic field scans was observed, establishing Mn$_{30}$ as a new SMM, the largest to date. Fig. 2 shows typical hysteresis loops, with the field applied approximately along the easy axis of magnetization. The blocking temperature is about 1.2 K, and the coercivity increases with decreasing temperature and increasing sweep rate, as expected for the superparamagnet-like behavior of a SMM. The loops do not display step-like features characteristic of resonant QTM between the energy states of the Mn$_{30}$ molecule, as observed for several other SMMs [6, 7, 8, 9, 10, 11, 12]. However, it is possible that steps are present but smeared out by broadening effects due to a distribution of magnetization relaxation barriers (i.e. $D$ values), consistent with the distribution of Mn$_{30}$ environments resulting from the disordered CMe$_3$ groups and solvent molecules observed in the crystal structure. It is thus not possible to determine directly from the hysteresis loops whether resonant QTM is occurring in this large Mn$_{30}$ molecule. Nevertheless, the first indication of quantum tunneling is the temperature dependence of the hysteresis loops below about 0.3 K (Fig.2). Detailed measurements of the hysteresis loops show however that the loops are still time-dependent below 0.3 K. This is presented in the inset of Fig. 3 showing the temperature dependence of the coercive field at different field sweep rates. The strong time-dependence in the temperature-independent regime is another important indication of QTM.

QTM can also be confirmed with magnetization decay studies. The magnetization was first saturated at 5 K with a large applied field, the temperature decreased to a chosen value, and then the field removed and the magnetization decay monitored with time. This provided magnetization relaxation rates $\Gamma$ at different temperatures allowing us to make an Arrhenius plot (Fig. 3) that is based on the Arrhenius law:

$$\Gamma = \Gamma_0 e^{-(U_{\text{eff}}/k_B T)}$$

where $\Gamma_0$ is the pre-exponential factor, $U_{\text{eff}}$ is the mean effective barrier to relaxation, and $k_B$ is the Boltzmann constant. The slope in the thermally activated region
tunneling is now only between the lowest QTM step at $H = 0$ in the loops of Fig. 2. Since the rationalizes the appearance at these temperatures of a 0.2 and 0.3 K. The ground state tunneling at levels. The crossover temperature between thermally ac-

The half-width of the hole of about 20 mT is larger than the hyperfine field (about 10 mT), reflecting the influence of dipolar couplings. A classical system or a quantum system with a continuum of levels would not show a hole but a monotonic increase for $H < H_{\text{dig}}$, indicated schematically by the dotted lines.

Additional confirmation of QTM in Mn$_{30}$ was obtained from the ‘quantum hole-digging’ method [20, 21, 22, 23]. This is a relatively new method that can, among other things, establish whether resonant tunneling occurs even when steps are absent in hysteresis loops due to a distribution of energy barriers. The method is based on the simple idea that after a rapid field change, the resulting magnetization relaxation at short time periods is directly related to the number of molecules in resonance at the applied field; Prokof’ev and Stamp proposed [20] that this short time relaxation should follow a $\sqrt{t}$ ($t = $ time) relaxation law. Thus, the magnetization of the Mn$_{30}$ molecules in the crystal was first saturated with a large negative field, and then a ‘digging field’ $H_{\text{dig}}$ of 0.275 T was applied at 0.04 K for a chosen ‘digging time’ $t_{\text{dig}}$. If QTM can occur in Mn$_{30}$, then that fraction (and only that fraction) of the molecules that is in resonance at $H_{\text{dig}}$ can undergo magnetization tunneling. After $t_{\text{dig}}$, a field $H_{\text{probe}}$ is applied and the magnetization relaxation rate is measured for short time periods; from this is calculated the short-time relaxation rate $\Gamma_{\text{sqrt}}$, which is related to the number of Mn$_{30}$ molecules still available for QTM [10]. The entire procedure is then repeated at other $H_{\text{probe}}$ fields. The resulting plot of $\Gamma_{\text{sqrt}}$ versus $H_{\text{probe}}$ reflects the distribution of spins still available for tunneling after $t_{\text{dig}}$, and it will display a ‘hole’ if resonant QTM did indeed occur during application of $H_{\text{dig}}$ for time $t_{\text{dig}}$. The obtained plot for Mn$_{30}$ (Fig. 4) does show a hole in this distribution, corresponding to a depletion of those spins that were in resonance and able to tunnel during $t_{\text{dig}}$ at $H_{\text{dig}}$. The occurrence of resonant QTM in Mn$_{30}$ is thus confirmed, since a classical system or a quantum system with a continuum of levels will not show a ‘quantum hole’ but rather a depletion of all spins with low barriers (Fig. 4).

The above results unambiguously demonstrate that Mn$_{30}$ undergoes tunneling, involving the coherent reversal of about 600 interacting electron spins within the Mn/O magnetic core. Of the three diagnostic tests for resonant QTM, Mn$_{30}$ clearly demonstrates two of them, temperature-independent relaxation and quantum hole digging. The third is steps in hysteresis loops, but these are broadened beyond resolution by the distribution of barriers ($D$ values) resulting from a distribution of Mn$_{30}$ environments. Mn$_{30}$ thus represents the largest SMM by far to unequivocally demonstrate QTM, establishing
that quantum effects can be clearly observed, and studied, even in very large 'magnetic particles' with dimensions approaching the mesoscale. This is made possible in Mn$_{30}$ by its monodisperse nature and highly ordered arrangement within the crystal (notwithstanding the solvent and CM$_3$ disorder, which in an absolute sense is a small perturbation), which prevent complications from distributions of particle size, shape, surface roughness, and spin. The latter have severely hampered previous attempts to demonstrate QTM in large magnetic particles, both for classical magnetic materials such as Co metal and molecules such as the ferritin protein. The results have consequently usually been negative, unclear or controversial $[25, 26, 27, 28, 29]$. In contrast, the present work demonstrates that crystalline assemblies of monodisperse molecular nanomagnets allow clear observation of quantum properties under straightforward conditions even for large systems approaching the mesoscale, the hydrocarbon shell of organic groups in Mn$_{30}$ ensuring the Mn/O cores are exactly identical in every molecule.

From a broader point of view, the present work confirms that large SMMs can be prepared and studied as crystalline assemblies of monodisperse particles. Mn$_{30}$ is much bigger than other currently known SMMs such as Mn$_{4}$, Mn$_{12}$, etc, and thus represents proof-of-feasibility of extending to larger species the many advantages of SMMs over classical magnetic particles. These include monodispersity, crystalline order, room-temperature solution synthesis, true solubility (rather than colloidal suspension) in common organic solvents, and an insulating shell of organic groups around the magnetic core, which additionally can be varied at will using standard synthetic chemistry methods. Such factors are clear benefits for the many proposed applications of SMMs, for example as qubits in quantum computing $[12]$, where the larger is an individual SMM, the easier it should be to manipulate and measure its quantum state. The synthetic variation of the hydrocarbon shell can also provide a facile way to increase (or decrease, if desired $[30]$) the isolation of a single SMM from its neighbors, and perhaps thus also help decrease decoherence problems.

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