# Quantum Effects in Single Molecule Magnets

*NSF NIRT Grant 0103290*

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## Introduction

This NIRT project focuses on magnetism at the nanoscale and materials known as single molecule magnets (SMMs). SMMs consist of a core of strongly exchange-coupled transition metal ions that collectively have a very large magnetic moment per molecule [1], thus far up to approximately 26 Bohr magnetons (or 26 times the electron spin). They have a strong (Ising-like) magnetic anisotropy that leads to an energy barrier to magnetization reversal. SMM crystals have a number of advantages over other types of magnetic nanostructures. Most importantly, they are monodisperse—each molecule in a crystal has the same spin, orientation, magnetic anisotropy and atomic structure. They thus enable fundamental studies of properties intrinsic to magnetic nanostructures that have previously been inaccessible, such as quantum tunneling of magnetization (QTM).

## Project Objectives

Our objective is the synthesis and characterization of SMMs to understand and control their quantum properties. Specifically, our goals are to:

–Investigate the fundamental mechanisms of QTM
–Study how molecular environments modulate magnetic anisotropy and QTM
–Engineer the exchange coupling between SMMs units in a crystal
–Synthesize half-integer SMMs with no nuclear spins, (i.e., I=0 for the metal ions)
–Identify new SMMs to try to increase their "blocking" temperatures, the temperature below which they can be magnetized and exhibit magnetic hysteresis
–Discover ways to disperse SMMs on a surface and attach them to a functionalized surface or polymer
–Determine the coherence times of electronic spins in SMMs.

Our approach is to combine the synthesis of new SMM materials with a wide range of advanced magnetic material characterization techniques. This includes quantum level specific probes such as high field EPR and NMR as well as high sensitivity (high field) magnetic measurements and other methods, available to the team via collaborations. The latter includes the low temperature micro-SQUID technique in collaboration with Dr. Wernsdorfer at the CNRS in Grenoble, France.

## Major Findings

We have made several major research findings this year. An important observation was recently reported in *Nature*, *416*, 406-409 (2002). Exchange-biased quantum tunneling was observed for a supramolecular dimer. Two S = 9/2 $Mn_4$ SMMs are dimerized by virtue of hydrogen-bonding contacts and a Cl···Cl van der Waals interaction. The weak antiferromagnetic exchange interaction (J = +0.1 K for $\hat{H} = J\hat{S}_1 \cdot \hat{S}_2$) between the two S = 9/2 SMMs has a large influence on the quantum properties of the dimer. Each half of the $[Mn_4]_2$ dimer acts as a field

bias on its neighbor, shifting the tunneling resonances observed as steps in the magnetization hysteresis loop. There is no step at zero external field as found for other SMMs. The absence of tunneling at zero field is important if SMMs are to be used for information storage. We are quite excited about this finding and are trying to prepare several other supramolecular assemblies of SMMs exhibiting exchange biasing. In fact, we have recently succeeded in synthesizing a $Ni_4$ S=4 SMM in which the intermolecular exchange coupling is tunable.

The preparations and characterizations of several new SMM polynuclear complexes were carried out. Two new $Mn_4(hmp)_6$ SMM complexes were reported, as well as a completely new $Mn_{12}$ type SMM complex. Success was made in preparing larger polynuclear Mn SMMs. Several complexes with the composition $Mn_{18}$ were made for the first time. One of the complexes has a S = 13 ground state and exhibits hysteresis in its magnetization versus magnetic field response. One SMM has been prepared with an $Mn_{30}$ composition. This is the largest SMM polynuclear manganese complex. Preliminary data show that it has a S = 7 ground state.

**EPR Investigations**. We have compared high frequency single crystal EPR data for monomeric and dimeric $Mn_4$ complexes where, in the case of the latter, intra-dimer exchange interactions are known to significantly alter the low temperature quantum behavior. The monomeric system exhibits typical single-molecule $S = 9/2$ EPR spectra; analysis of these data have enabled us to characterize the effective spin Hamiltonian parameters for this material. In the dimeric system, the ground state transition shows a splitting over a narrow range of fields and frequencies. The transfer of spectral weight between these split peaks is consistent with the exchange bias picture which has been developed to explain the absence of a zero-field tunneling resonance in low temperature hysteresis experiments[2]. Indeed, these measurements provide the first independent confirmation for this exchange bias model. The absence of a significant intensity in excited state EPR transitions for the dimer contrasts to the results for the monomer. This likely suggests important differences concerning the coherence of excited states of the dimer versus the monomer. No clear indications for intermolecular exchange interactions were observed in the EPR for the monomer.

As a follow up to earlier experiments on $Mn_{12}$-Ac with the magnetic field applied along the easy axis[3], we have carried out detailed angle dependent studies with the field in the hard plane. In addition to a precise determination of the quartic zero-field interaction, we observe an angle dependent linewidth and splitting of the hard plane EPR peaks which we attribute to the recent model of Cornia *et al.*,[4] whereby local rhombic distortions are caused by disorder associated with the ligands. In addition, these investigations have resolved a long standing dilemma concerning the origin of the anomalous resonances reported in Reference [3], which are shown to be due to an excited state with $S = 9$ characteristics.

**Magnetometry Studies.** We studied QTM in the SMM $Mn_{12}$-ac using high sensitivity magnetic measurements in a new vector high field superconducting magnet system. Despite years of careful investigations of the magnetic properties of this prototype and most studied SMM, the origin of MQT has remained, until now, poorly understood. This was due to the fact that the magnetic properties do not reflect the tetragonal symmetry of the molecule and that experiments indicate a distribution of tunneling rates[5]. The new vector magnet system has enabled the first study of the symmetry of the magnetic response in this material. We have demonstrated that an average crystal 4–fold symmetry is due to local molecular environments of 2-fold symmetry that are rotated by 90 degrees with respect to one another, confirming that solvent disorder which

lowers molecule symmetry is at the origin of QTM. As mentioned above, this was proposed by Cornia et al.[4] based on a x-ray diffraction data. Further, we have magnetically distilled a SMM crystal to study a subset of these lower (2-fold) site symmetry molecules and found evidence for a spin-parity effect consistent with a local 2-fold symmetry. These results highlight the importance of subtle changes in molecule environment in modulating magnetic anisotropy and QTM.

**NMR Studies**. These studies are being carried out at NHMFL, since they need special NMR equipment that is only available there. The reason is that the NMR signals from the SMMs are too broad to be observable with commercially available NMR spectrometers. For example, the $^{55}$Mn NMR peaks from $Mn_{12}$-Acetate have widths on the order of 30 MHz, while the range covered by commercial spectrometers is at most 100 kHz. At NHMFL, we succeeded in observing $^{55}$Mn NMR peaks from $Mn_{12}$-Acetate, $Mn_{12}$-benzoate and $Mn_{12}$-fluorobenzoate. These measurements revealed for the first time that the Mn ions in the benzoate-containing compounds have four different Mn sites, as compared to only three in the standard $Mn_{12}$-Acetate compound. Each spectrum needed signal averaging for about 24 hours, and the signals were detectable only below the blocking temperature (about 2.7 K). Parallel studies of carbon-13 and Mn-55 NMR at NHMFL in Tallahassee have provided the first direct evidence for the delocalization of the electronic spin onto the organic framework in Mn12-Ac. This observation is complementary to the Hill group's EPR results, and suggests a pathway for intermolecular exchange and a new avenue for the magnetization tunneling[6].

In just one year, this NIRT team has managed to solve the long standing (~6 year) problem concerning the microscopic origin of the transverse interactions (tunnel splitting) responsible for the tunneling in $Mn_{12}$-Ac, through a combination of magnetic and spectroscopic investigations. More importantly, however, through studies of a range of SMMs unique to this team, a clear picture is beginning to emerge concerning the influences of distinct molecular species and the role of inter-molecular exchange interactions. In particular, it has become abundantly clear that the $Mn_{12}$Ac system is far from ideal in terms of studying the fundamental properties of molecular nanomagnets. Our future plans involve an extensive array of alternative high spin SMMs that are only available to this NIRT team.

## Educational and Outreach Activities

Graduate, undergraduate students and postdoctoral fellows have received interdisciplinary research training as a direct consequence of this project, thus far, 5 undergraduates, 12 graduate student and 3 post-docs. Two symposia this Fall have highlighted our research accomplishments and this Fall's MRS meeting featured a tutorial lecture by Hendrickson on SMMs.

**References**

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