The Effects of Variants in Mn$_{12}$ac

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In this experiment Electron Paramagnetic Resonance (EPR) is used to study Manganese 12 acetate. There is a brief overview of Single Molecule Magnets (SMM) and an explanation of the theory behind the variations in the Mn$_{12}$ac system. A magnetic field was applied to the system and the quantum tunneling that resulted was studied. This was done at different angles to give a clear picture of the system; then these data were analyzed for any evidence of variants in the molecules. The evidence backs up the conclusion that there are variants in the Mn$_{12}$ac molecules, and these variants cause minor peaks (shoulders) as well as the major peak where most of the molecules tunnel.
**Introduction**

Single Molecule Magnets (SMM) have recently become an area of interest to physics. [1, 2] Magnets are used as information storage devices, but these magnets have size as a limiting factor. The magnets can only be made so small before the magnetic field will fluctuate at room temperatures rendering them unusable as storage devices. [1] A Single Molecule Magnet is a material that has properties that are both classical and quantum in nature, and as such could be used for quantum computing where the information is handled in such a way that the quantum effects of the material can be utilized. [1,2]

In 1993 the first SMM was created, \([\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4]\cdot2\text{CH}_3\text{COOH}\cdot4\text{H}_2\text{O} (\text{Mn}_{12}\text{ac})\) (see Fig. 1), and it has a ground state of \(S = 10\) [1,2]. The ground state of \(S = 10\) comes from the antiferromagnetic interaction between the \(S = 3/2\) spins of Mn\(^{\text{IV}}\) ions and the \(S = 2\) spins of Mn\(^{\text{III}}\) ions. The \(S = 10\) state is split into 21 levels because of the axial zero-field splitting. The levels are characterized by the quantum number \(m_s\), where \(-S \leq m_s \leq S^2\). The energy of each level is determined by

\[
E(m_s) = -|D|m_s^2 + g \mu_B B m_s, \quad (1)
\]

where \(D\) is the axial zero-field splitting parameter. The Hamiltonian used to describe this system is

\[
\hat{H} = D\hat{S}_z^2 + E(\hat{S}_x^2 - \hat{S}_y^2) + \mu_B \vec{B} \cdot \vec{g} \cdot \hat{S} + \hat{O}_4 + \hat{H}', \quad (2)
\]

where \(\hat{O}_4\) is the crystal field, and \(\hat{H}'\) is the environmental couplings [3].

One of the quantum effects seen in Single Molecule Magnets is quantum tunneling. In SMM’s there is thermally assisted quantum tunneling and magnetic
quantum tunneling (MQT). Thermally assisted quantum tunneling occurs when there is enough thermal energy to cause tunneling. Magnetic quantum tunneling occurs when the axial symmetry is broken [3]. When this does not occur the degenerate levels are off resonance, or they do not line up. Due to the wave nature of the molecule, when a sample of molecules is taken and observed, tunneling occurs in a minority of the molecules off resonance, but strong peaks occur at the resonant points.

Another observation about Mn12ac is that the hysteresis loop is not a smooth figure, but has steps in it (see Fig. 2). The steps are locations where tunneling is occurring, and for tunneling to occur the symmetry must break, an action for which a cause is not clearly known [3]. One theory of this is a discrete disorder due to the acetic acid during crystallization. For the molecule to be ordered with no variations it must have a four-fold symmetry ($S_4$). The discrete disorder theory suggests that there are six variations in the basic model of Mn12ac, four of which have symmetry lower then $S_4$. This model suggests that the disorder would allow for locally varying rhombicity, or E strain, and therefore there would be a distribution in the tunnel splitting [3]. With this model it is predicted that three of the variants, $n = 1$, $n = 2$ trans, and $n = 3$, make up 62.5% of the molecules, with the fourth variant, $n = 2$ cis, accounting for about 25%. Therefore, the measurements as a function of field orientation in the hard plane could be due to the E strain caused by the variants [3]. The focus of the research conducted was to further verify this theory.

**Equipment and Procedure**

The research was conducted using a high frequency single crystal electron paramagnetic resonance (EPR). The measurements were carried out using a millimeter-
wave vector network analyzer (MVNA) and a high sensitivity cavity perturbation technique. The magnet used was a split-pair magnet with a 6.2 T horizontal field and vertical access [3]. The MVNA is used as a spectrometer; it is a device that allows vector measurements with continuous frequency coverage from 8 to 600 GHz. The cavity perturbation is a cylindrical cavity where the sample is placed. There are variations on this cavity. The one used in this experiment was able to rotate in two planes of direction (Figure 3 and 4). The probe is a long wave guide made from copper and stainless steel, the rotating cavity is placed at the end of it [4]. The wave guides are attached to Schottky diodes; in turn coax cables are attached to these diodes. The Schottky diodes multiply the frequency, and at one end there is the harmonic generator, the output end is the harmonic mixer [4]. The first signal $S_1$ goes to the harmonic generator and the frequency gets multiplied; then the signal goes to the cavity and in turn travels up the other wave guide to the harmonic mixer. Then signal one and signal two are combined in the harmonic mixer. The equation $\Delta f = NF_1 - NF_2 = F_{mm} - NF_2$, gives the beat frequency, where $F_1$ is the frequency that travels through the cavity, and $F_2$ is the reference frequency. The synthesizer keeps the beat frequency constant, and the receiver gets the information from the beat frequency. The two signals are combined and from that the data are collected and stored on a computer, along with other data, such as the magnetic field and the temperature.

The Mn$_{12}$ac is then placed in the cavity and put into the system. This is the most crucial part of the setup. After the crystals have been removed from the solution, there is only a small window of time before the solution evaporates and the crystal degenerates so that it cannot be used. Also the crystal has to be placed in the cavity so that the magnetic
field will be at approximately 90º to it initially. The resonance peaks are then found and the system is tuned so that there is little background noise. Then the experiment can begin. Some sample sweeps are taken to determine the basic look of the system and to approximate where the field is perpendicular to the sample. This is done to make sure that the sample is in there to within a degree of 90º. Then data are taken at many angles in a particular plane; then the plane is moved and the test is repeated so that the whole system can be analyzed.

**Results**

The original goal of this research was to reconfirm the existence minor peaks in the Mn_{12}ac system, in order to provide evidence that there are variations of each Mn_{12}ac molecule and that these variations do have an effect on the resonance peaks. To accomplish this, the sample was studied at 2 K at several dial positions (angles in the hard axis). The dial positions were Dial 1000, 1171, 1342, 1513, 1684, 1855, 0026, and 500. Dial position 500 was the test position, and does not really fit in with the other data, so it will not be used in the analysis.

To determine the structure of the system, the individual data file, which include an up or down sweep of the molecule from one field to another at a particular angle, were analyzed. The background noise was subtracted out, the graph was flipped so that the peaks were easier to look at, and then the graph was interpolated so that there were a uniform number of points to be used in a matrix. For this experiment 1000 points were interpolated. Then the interpolated files were put into a matrix, this produced a graph where the peaks were clearly defined (Fig. 5). This was done for every dial position (angle in the hard axis); then the 90º angle was found and the graph was changed
accordingly. The 90º angles for each dial were then plotted with each other, (Fig. 5). This shows the angle dependence of the molecule, and shows how the shoulders (minor peaks around the major peak) appear and disappear where there should only be peaks.

Another analysis was done with these data was the points for the largest pea. The data was taken from the matrix for a particular field. Several of these data points were taken around the same area and plotted. Fig. 7 shows how the intensity of the shoulders differs from each other and the major peak. For the plots that did not have any shoulders, just the major peak was graphed in this manner.

The last analysis done on this system involved doing a simulation. The simulation was conducted with the Gamma angle equaling 0º and 90º (Fig. 8). Then a comparison of the simulation was made with the actual data. The peaks occur around the same place, which confirms the validity of the experiments.

**Discussion**

The experiment confirmed the existence of shoulders (minor peaks adjacent to a major peak) in the Mn$_{12}$ac system. The graphs clearly indicate that there are minor peaks around the major peak at certain angles, and that the shoulders increase and decrease in intensity according to the angle of the magnetic field. This is evidence that the Mn$_{12}$ac system does indeed have variations in the molecule.

The intensity of the minor peaks also provides evidence of the variation theory. Although there is a possibility for six variants, because of the way they interact three peaks appear. The majority of the variations occur at the major peak, where most of the electrons tunnel, but the other variants that do not tunnel at those resonance points account for the shoulder around the peak. The small shoulder roughly corresponds to the
lower number of variants that will tunnel at that resonance, and the angle dependence is clearly shown so one variation tunnels better at some angle than the other variation, thus accounting for the variations in intensity of the shoulders.

The simulations that were conducted also corresponded with the major peaks (the simulation assumes four fold symmetry, and as such the shoulders would not appear in the simulation). The major peaks do correspond with the major peaks in the experimental data, verifying the results of the experimental data.

This experiment did provide valuable evidence that there are variations in the symmetry of the individual \( \text{Mn}_{12}\text{ac} \) molecules, as opposed to former thinking that they are all alike. \( \text{Mn}_{12}\text{ac} \) has been studied almost exclusively because of the four fold symmetry and all of its molecules being alike. One of the important aspects for a SMM to be utilized in quantum computation is that all of the molecules are exactly alike, but the discovery of these shoulders, giving evidence to the existence of variations in the molecules, means that \( \text{Mn}_{12}\text{ac} \) is not a good candidate for use in quantum computation devices. Future research should be dedicated to studying other SMM systems to determine if they could be utilized for such a purpose. Also, just because the \( \text{Mn}_{12}\text{ac} \) system cannot really be utilized for the quantum computation purpose does not mean research on the system should stop, because another use for the system could present itself in the future.

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References


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FIGURE 1. Model of Mn$_{12}$ac.
FIGURE 2. Hysteresis loops showing the steps associated with quantum tunneling.
FIGURE 3. Drawing of the MVNA.

FIGURE 4. Drawing of the cavity used.
FIGURE 5. Contour plot of the Mn$_{12}$ac system showing the shoulders.

FIGURE 6. Center of the peaks (at 90 degrees) for all of the dial positions.
FIGURE 7. Slices through the contour plot corresponding to the shoulder and high peak region.

FIGURE 8. Simulation figure.