

High Frequency Electron Paramagnetic Resonance Studies of Mn₁₂ Wheels

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Abstract

High Frequency Electron Paramagnetic Resonance (HFEP) experiments were conducted on dimeric Mn₁₂ wheels to determine the physical properties of the molecule. Angle dependence experiments were used to determine the molecule's physical orientation with respect to an external field, temperature dependence experiments were conducted to gain insight into the interactions within the dimer, and frequency dependence experiments were conducted to experimentally deduce what the energy level diagram for this specific molecule looks like.

Introduction

Computing technology is constantly changing and as it evolves, the search for smaller units of memory and faster processing capabilities becomes exponentially more important. Scientists use two approaches to developing smaller magnetic units: The top-down method and the bottom-up method. The former encompasses any efforts to simply reduce the size of bulk magnets, while the latter revolves around the idea that one can synthesize molecules, ideally one miniscule magnetic center at a time. Single-Molecule Magnets (SMMs) are candidates for the bottom-up method [1-3]. At low temperatures the SMMs are blocked in a certain spin state (up or down) and therefore show potential as magnetic memory units. SMMs are orders of magnitude smaller than the current bulk magnets, and many systematic ways are being developed to construct and modify these SMMs.

SMMs are also of great interest because they are small enough to exhibit quantum characteristics as well as classical ones. Although SMMs are blocked in a certain spin state at low temperatures, this magnetization always disappears after some time due to quantum tunneling between energy states. While this tunneling may be detrimental when attempting to use SMMs as memory storage, it is a necessary trait for the quantum bits in quantum computing. This characteristic has led people to suggest that if this magnetic relaxation of SMMs could be controlled, SMMs could eventually be used as the quantum bits in quantum computing and revolutionize current computing standards [2].

Currently, inorganic chemists are producing more and more compounds that can act as SMMs, and physicists are conducting experiments on these various compounds to determine their physical properties [3]. These single molecule magnets usually are comprised of several transition-metal ions connected by various organic ligands. Each of these metal ions have

intrinsic spins, and these spins interact with one another either ferromagnetically or antiferromagnetically [1,3]. The spin for the entire molecule is approximated using a giant spin approximation. This approximation is found simply by summing up the vector for the spins of each ion. If they interact ferromagnetically, all the ions have spins pointing in the same direction. If they interact antiferromagnetically, all the ions have some spins pointing in one direction and some pointing in the other direction. In nature, substances tend to prefer antiferromagnetic coupling; therefore, when chemists are creating new SMMs it is easier to have antiferromagnetic molecules. If all the spins cancel out, though, there will be no net magnetic moment. SMMs are useful because they have such high spin numbers and therefore large magnetic moments. Most SMMs are antiferromagnetic, but they are a special case of antiferromagnetism called ferrimagnetic coupling. If the spins interact ferrimagnetically, then the spins point in opposite directions but are of varying magnitude and the molecule therefore still has a net spin. The large spin numbers stemming from the transition-metal ions they are comprised of constitutes an important and defining characteristic of SMMs.

Another significant property of SMMs is the property that gives rise to the blocking, the uniaxial magnetic anisotropy [1]. This anisotropy defines a specific energy barrier that must be overcome in order to change from “up” spin to “down” spin or vice versa. For single molecule magnets this magnetic anisotropy barrier, U , can be relatively large giving rise to magnetic hysteresis, below a characteristic blocking temperature, reminiscent of classical magnets. The difference, however, is that the magnetization dynamics of SMM crystals are heavily affected by quantum effects as well. Figure 1 shows this magnetic anisotropy barrier.

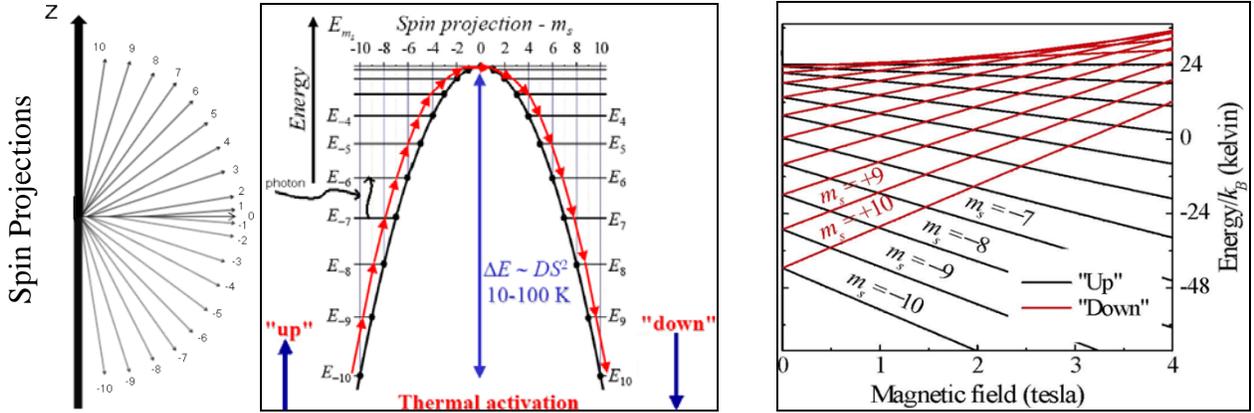


Figure 1. (left) Energy levels corresponding to the different spin projections of an S=10 system. In EPR experiments, absorption of a photon with certain energy excites the spin to the next spin projection. The energy barrier between degenerate spin states (up and down spins with the same energy) is given by DS^2 . (right) Variation of the energy of each spin projection in an applied magnetic field, illustrating the Zeeman effect.

The intrinsic quantum properties of these SMMs can lead to tunneling between spin states and subsequently give rise to an effective energy barrier, U_{eff} , that is significantly less than the apparent magnetic anisotropy barrier U . This energy barrier is given by the equation $U = DS^2$. The energy for each individual spin projection is given by $E_{m_s} = Dm_s^2$, where m_s is the spin projection onto the uniaxial direction defined by the crystal (Fig. 1). When D is positive, the energy levels corresponding to spin projections with the lowest magnitude are most stable; when D is negative, energy levels corresponding to spin projections with the highest magnitude are most stable. A positive D value corresponds to easy-plane magnetic anisotropy, whereas a negative D value corresponds to easy-axis magnetic anisotropy [4]. If a system is approximated as a sphere, easy-plane anisotropy refers to a system that has an entire plane in the sphere that magnetic moment prefers to align with. Easy-axis anisotropy, however, refers to a system in

which there is only a single axis through the sphere that the magnetic moment prefers to align with. SMMs must have negative D values and therefore have an easy-axis and a hard-plane.

In a system with axial symmetry, the spin energy levels can be completely described with the equation $E_m = Dm^2$, but most systems are more complicated and less symmetric and require other terms to fully describe the energy levels. In order to deduce a value for the uniaxial magnetic anisotropy, as well as other terms in a more complicated system, high frequency electron paramagnetic resonance (HF-EPR) experiments are conducted on the SMMs. This spectroscopy is analogous to the visible spectroscopy used to observe the quantum states of atoms, but in this case the pertinent energy scale is relatively low (~10 Kelvin). This small energy scale requires radiation with a frequency in the microwave range (wavelengths in the millimeters).

For this project we conducted HF-EPR experiments on high-spin Mn_{12} -based wheel SMMs. These Mn_{12} wheels are dimeric molecular nanomagnets. In other words, the molecule is made up of two Mn_6 monomers. Each half of the molecule acts as an individual SMM with $S = 7/2$. The monomers couple ferromagnetically with each other giving the entire dimer $S = 7$. This coupling gives rise to an extra internal spin degree of freedom in the dimer, which results in complicated interactions not only in each half of the wheel, but in the entire wheel as well.

Figure 2 shows the molecular structure of the Mn_{12} wheel and where the spins are for each ion.

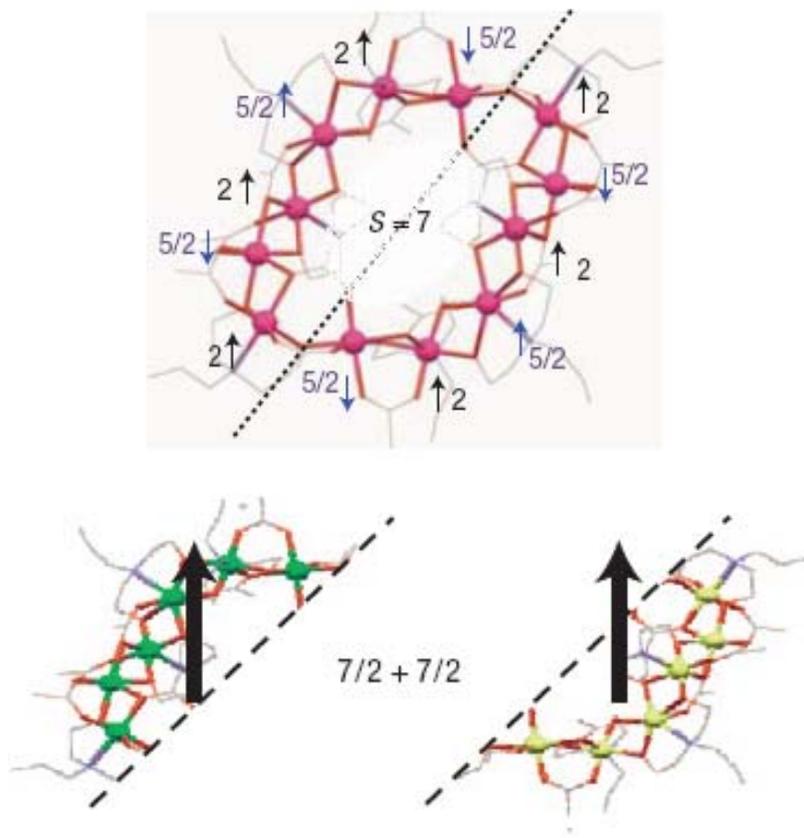


Figure 2. (Top) The giant spin approximation for the Mn_{12} molecule, the chemical structure, and the ferrimagnetic interactions between the ions. (Bottom) The dimer is comprised of two halves, each with $S = 7/2$ adding up to a total value of $S = 7$.

Through HFEPR experiments we will locate the hard-plane for this molecule and with that information deduce where the easy-axis is. Once the easy axis has been located and aligned with the external magnetic field, we will map out the molecule's energy level diagram with frequency dependent HFEPR experiments.

Electron Paramagnetic Resonance

Electron paramagnetic resonance is more generally termed electron spin resonance because it is a branch of spectroscopy that investigates changes in electron spins within the material undergoing the tests. Our experiments are called high-frequency electron paramagnetic resonance (HFEPR) because they are conducted at relatively high frequencies (as high as the THz range compared to conventional EPR experiments in the 10 GHz range) and because they investigate the spins of paramagnetic materials.

The simplest example of how EPR experiments work is a hypothetical single electron with spin $1/2$. In the absence of an external magnetic field, no difference exists between spin up or spin down with respect to energy. In other words, the electron has no preference for spin up or spin down. However, once an external magnetic field is applied, the electron's spin now prefers to point in the same direction. The once degenerate energy state now splits into two separate energy levels for either spin up (+1/2) or spin down (-1/2). This coupling between the spin and the external field is called the Zeeman effect [4]. The splitting of the energy levels from the Zeeman effect is given by

$$E_z = g\mu_B \vec{B} \cdot \vec{S} \quad (1)$$

or

$$E_z = g\mu_B B m_s \quad (2)$$

where E_z is the energy given by the Zeeman effect and μ_B , m_s , and g are all constants. Eq. (2) shows that the energy level varies linearly with B , the external magnetic field. Fig. 3 shows an example of what the splitting from the Zeeman effect might look like in a system with $S = 1/2$.

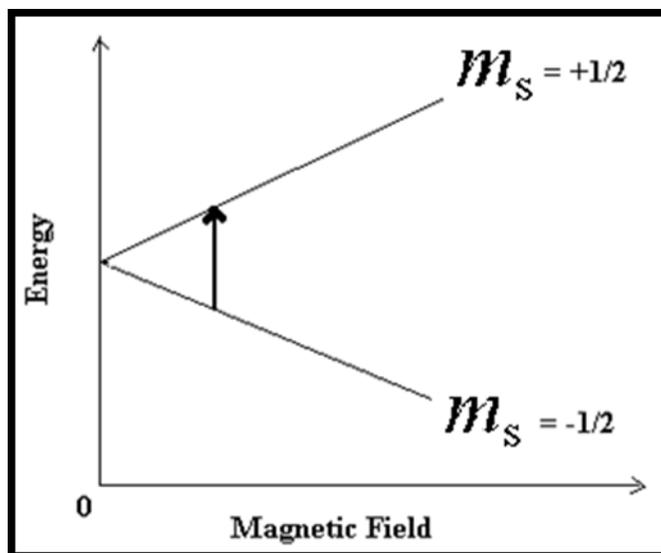


Figure 3. The splitting of the degenerate energy levels due to the Zeeman effect in a spin $\frac{1}{2}$ system. The arrow shows a hypothetical jump from one energy state to the other.

Because energy is directly related to frequency of radiation, the ordinate can also be in frequency units. These energy levels obey quantum mechanical restraints and therefore the system will remain in one state until it absorbs the right amount of energy to jump to the next energy level. So, in EPR experiments the sample under study is hit with radiation, and either the field or the frequency is tuned until the proper energy is absorbed and the spin state jumps to a higher energy level. The transmission of the radiation is recorded, and when the exact energy is reached for the spin to change energy levels, an absorption peak can be seen. These absorption peaks contain a lot of information about the sample and its energy level diagram.

The example of a free electron in EPR experiments is highly simplified, and there are often many different split energy levels with complicated crossings and repulsions. The EPR experiments are done on these complicated samples so that the absorption peaks at different frequencies and different fields can be seen and then simulated energy levels can be fit to the

experimental data to get an idea for the parameters of the spin Hamiltonian for the specific system being studied. Fig. 1 shows an example of what a more complicated system (spin 10) might look like.

The results from EPR spectra can also help us to determine how the sample is oriented with respect to the external magnetic field. We used EPR experiments to help locate the hard-plane and the easy-axis of the molecule being examined. We used angle-dependent EPR experiments. We swept the magnetic field with the sample at different orientations with respect to the external magnetic field and noted the locations of the EPR absorption peaks. The orientation at which the absorption peaks are highest in field is closest to the hard-plane, whereas the absorption peaks lowest in field are closest to the easy-axis. Fig. 4 is an example of this absorption spectra.

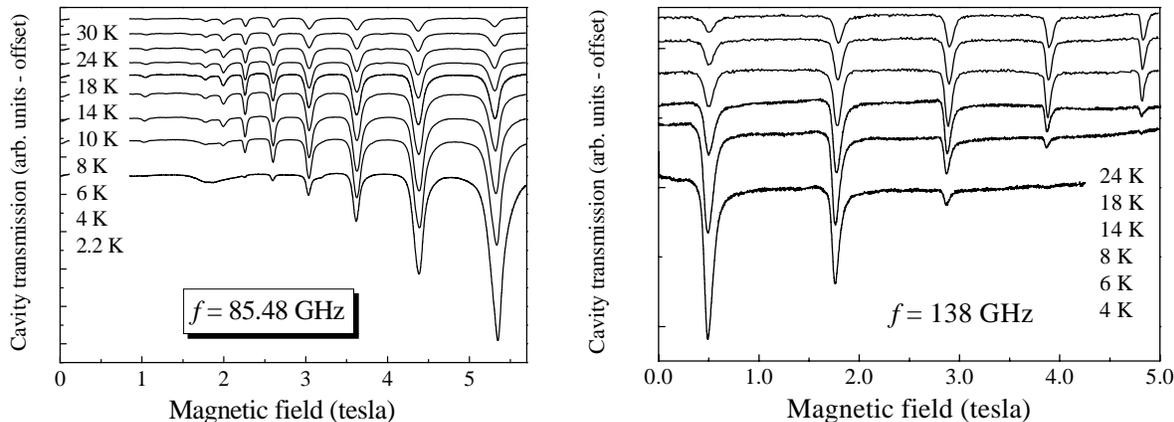


Figure 4. The absorption spectra for the same sample in two different physical orientations: (left) external magnetic field aligned with the hard plane; (right) external magnetic field aligned with the easy axis.

Experimental Setup

When conducting these experiments either the field can be swept while the frequency is held constant or vice versa. Our experimental setup only allows us to fix the frequency while we sweep the external magnetic field. This method is called narrowband. We must use this narrowband technique because of the waveguides used to propagate the microwave radiation to and from the sample and also because of the resonant cavity used to hold the sample. The waveguides prevent us from varying the frequency while keeping magnetic field constant because standing waves in the waveguide tubes would interfere with the incoming radiation if it were changing in frequency. The resonance cavity we use requires that we tune the frequency to a certain resonant frequency, thus preventing a broadband approach (sweeping frequency) to our EPR experiments.

For our HFEPR experiments we use an instrument called a millimeter vector network analyzer (MVNA). The MVNA is the instrument that produces the microwave radiation as well as the instrument that detects the returning signal after the radiation has passed the sample. The MVNA allows us to very precisely tune the frequency to a resonance mode for the cavity.

The cavity is located at the very end of a long probe so that it can be placed in the center of the magnetic field which is deep within a cryostat. We attach the cavity at the end of the waveguide tubes which have their other end connected to various diodes (depending on the frequency range) and eventually coaxial cables leading to the MVNA. The radiation comes from the MVNA through a coaxial cable, down a waveguide tube and to the resonant cavity. There the microwaves hit the sample and then go back up a waveguide tube back through a coaxial cable and back to the MVNA. This process goes on while we sweep the external magnetic field, thus allowing us to see the field at which a sample has absorption peaks for a certain frequency.

The external magnetic field is generated by a superconducting magnet within a cryostat. The cryostat keeps the superconducting magnet at liquid-helium temperatures. We used two different magnets for this experiment, a 7-T magnet and a 17-T magnet. Fig. 5 gives an illustration of the experimental setup.

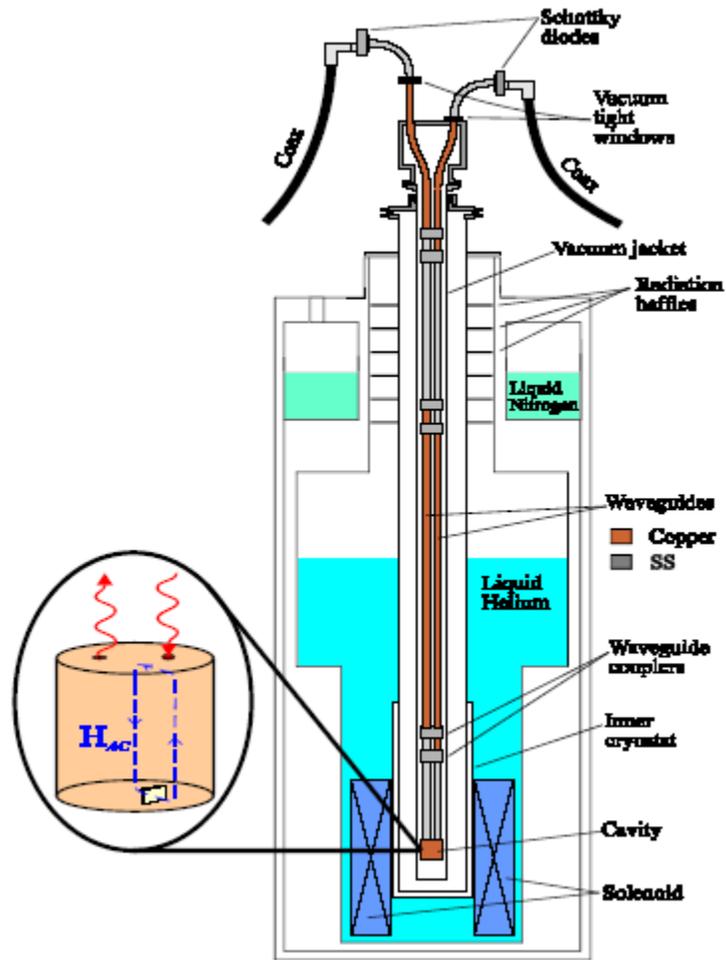


Figure 5. Overview of a cryostat, magnet, and probe.

Procedure

We use HFEPR experiments to deduce various physical properties of the SMM sample we are studying. In order to focus on specific properties we must be able to examine the EPR spectra's dependence when different variables are changed. The following sections describe different parts of the experiment that focus on how different variables affect the EPR spectra, and what those effects can tell us.

Angle Dependence

When beginning the experiment, we must first determine how the sample crystal is physically oriented with respect to the external magnetic field. We conduct angle dependent HFEPR experiments to do this. This means that while we do magnetic field sweeps, we fix the frequency and the temperature while changing the position of the sample. By isolating just that variable we can watch the effects that changing it has on the EPR spectra.

The 7-T magnet used for this part of the experiment has two degrees of rotation. A rotator allows us to rotate the plate that the sample is mounted on in one plane (the diode), and another rotator allows us to rotate the entire cavity (the motor) in a perpendicular plane. Using these two degrees of rotation, we can essentially map out an entire sphere and therefore examine any possible orientation of the sample.

We used these rotators to perform angle dependence experiments on the Mn_{12} wheels so that we could determine where the hard-plane was relative to our experimental setup. Once we found the hard plane we were able to find the axis perpendicular to the plane, the easy-axis. The method was to sweep 180° with the motor, move the diode 10° , sweep 180° on the motor again,

and so on until an entire hemisphere was mapped. An example of the data obtained from one of these angle dependent HFEPR experiments is shown in Fig. 6.

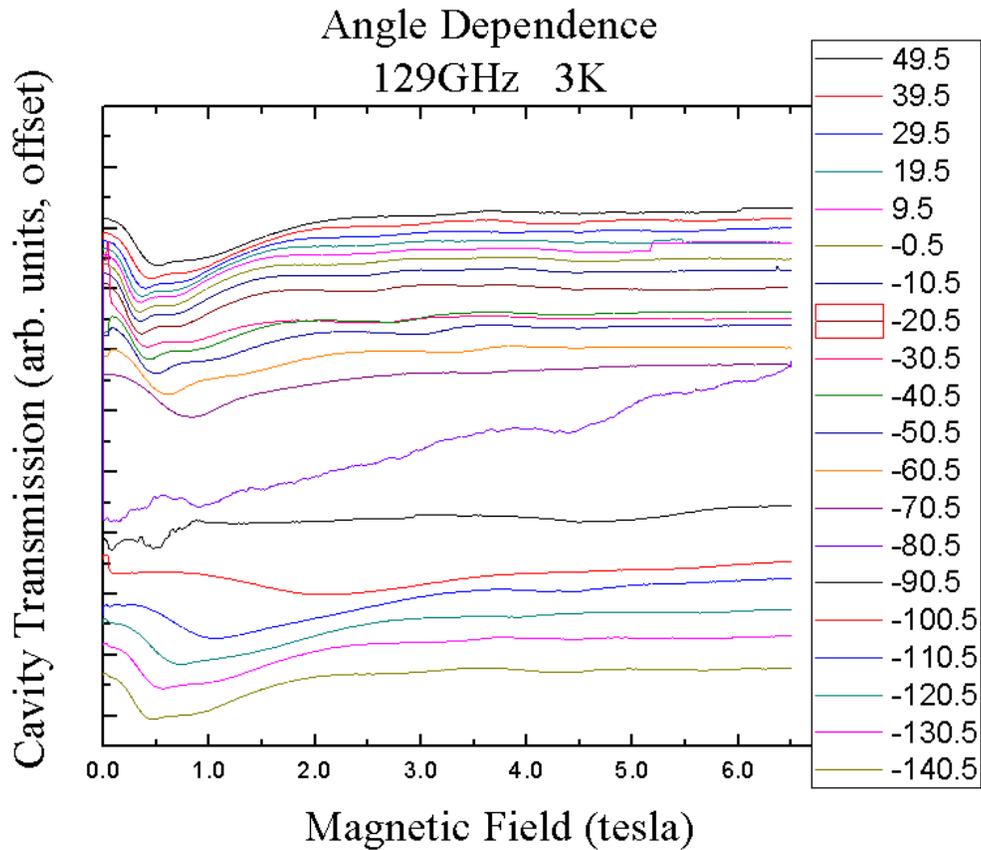


Figure 6. Data from an angle dependence experiment. As the sample is rotated the HFEPR absorption peak moves from higher field to lower field and back. The position at which the peak is at lowest field is closest to the easy-axis and the position at which the peak is at highest field is closest to the hard-plane.

Using the results found from these angle sweeps, we found the motor angle at which we were closest to the hard plane for each diode angle. When we connected each of these points, we had

a rough idea of where the hard-plane was. We then rotated the sample 90° away from the hard-plane and found the easy-axis.

Temperature Dependence

Once we were satisfied that the sample was oriented in such a way that the easy-axis of the Mn_{12} wheels was aligned with the external magnetic field, we conducted temperature dependence EPR experiments. These allowed us to examine a few different properties.

First of all, one can use temperature dependence EPR experiments to determine whether an observed absorption peak is a ground state or an excited state transition. When the temperature is lower, more spins are trapped in the ground state due to thermal limitations. As the temperature increases, more excited states become populated. This effect can be seen in the EPR spectra. If the peak is sharper for lower temperatures, then it is a ground state transition; if it gets sharper as temperature increases, it is an excited state transition. For this particular sample we expected to see a slope of the energy level corresponding to $g = 2$ along the easy axis. In order to test this hypothesis we do HFEPR experiments at various frequencies and plot frequency vs. field for where we see absorption peaks. These points should have the slope of an energy level corresponding to $g = 2$. It is important to know that if the peaks we observe are ground state transitions or excited state transitions before we plot them.

Secondly, we were interested in examining how each half of the dimer interacted with the other, which can also be observed in the temperature dependence experiments. The observed absorption peaks for the ground state transitions were double peaks. As the temperature was varied the relative intensities of each individual peak changed, as seen in Fig. 7. These results gave us some insight to the interaction between the halves of the dimer.

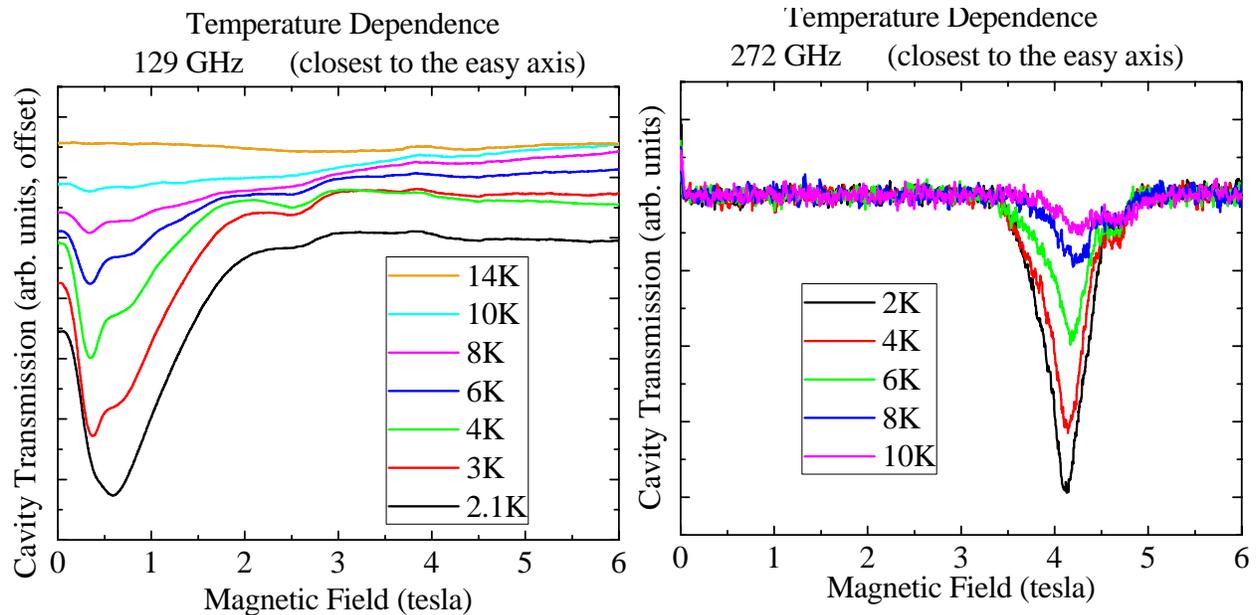


Figure 7. (left) Data from a temperature dependence HFEPR experiment performed at 129 GHz. As temperature increases the intensity decreases, implying that the absorption peak seen is a ground state transition peak. The graph also illustrates that as the temperature increases intensity shifts to the peak on the right because higher energy state transitions become a factor. (right) HFEPR data taken at a higher frequency (272 GHz). Once again, this is a ground state transition peak with the intensity decreasing and shifting to the right as temperature increases.

Frequency Dependence

As mentioned before, we hoped to experimentally find how the energy levels behave with respect to a changing external magnetic field. We do this with frequency dependent HFEPR experiments. We keep all of the variables constant and sweep the magnetic field at different frequencies. We then plot each of the peak positions on a frequency vs. magnetic field graph and use a simulation program to fit energy levels to the peak positions.

Results

After we aligned the sample so that the easy-axis was parallel to the external magnetic field, we conducted frequency dependent HFEPR experiments as well as temperature dependent HFEPR experiments at each frequency. Fig. 8 shows peak frequency positions versus magnetic field.

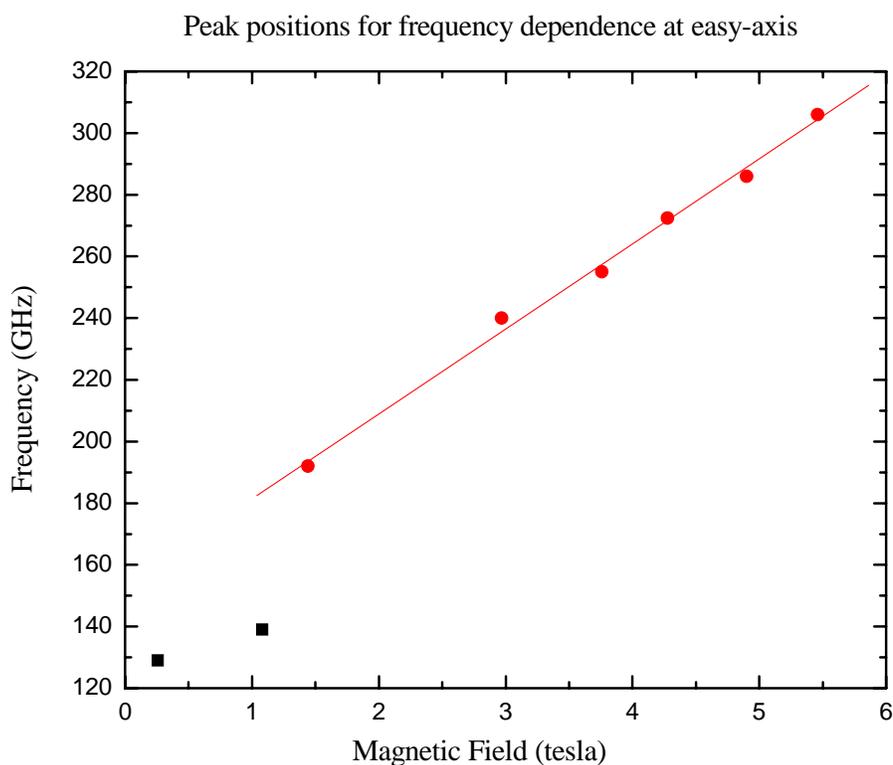


Figure 8. Peak frequency versus magnetic field for HFEPR experiments at low temperature.

The linear fit is an approximation of how the energy level behaves with respect to field.

The slope of the line shown in Figure 8 is 27.6. The expected slope for $g = 2$ is 28. The fact that our experimental value is so close to the predicted value reaffirms that we are on the easy-axis.

Conclusion

The results shown in Fig. 8 imply that these Mn_{12} wheels are relatively complicated. Our experiments were unable to find any frequencies between 140 GHz and 190 GHz. We were therefore unable to fully interpret our results. It appears that there are two different branches in Fig. 8. This characteristic could be due to crossing of energy levels or energy level repulsion.

In order to completely determine what we are seeing, we need to perform further HFEPR tests. It is important that we find frequencies in the 140-190 GHz range and fill the gap in data that we have now, as well as perform HFEPR experiments at frequencies lower than 110 GHz. Once we are able to fill in this data and find more points to put on the graph shown in Fig. 8, we may have a clearer picture of what is occurring in the system.

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