Electron Paramagnetic Resonance in a Holmium based Single Molecule Magnet

Lisa Friend1,  Sanhita Ghosh2,3, Christopher Beedle3 and Stephen Hill2,3
1Manatee Academy Middle School, Port St. Lucie, Florida 34986, USA
2Department of Physics, Florida State University, Tallahassee, Florida 32306, USA
3National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL 32310, USA

Electron Paramagnetic Resonance (EPR) Spectroscopy

EPR is a spectroscopic technique that detects the transitions of unpaired electrons in an applied magnetic field. Absorption peaks occur in a spectrum when the magnetic field tunes the two electron spin states so that their energy difference matches the radiation energy.

In an applied magnetic field a free electron will precess about the field at a frequency that is contingent on the magnitude of the applied field. When the frequency of the source radiation matches the precession frequency, the electron will absorb energy and move to higher energy states, shown as absorption peaks.

Zeeman Effect: Splitting of a spectral line into components in the presence of a magnetic field due to the lifting of degeneracy of electronic energy levels

Hyperfine Coupling: Interaction of electron and nuclear spins giving rise to additional allowed energy levels and thereby leading to splitting of EPR peaks

Resonant cavity and waveguide assembly
- Frequency range: 50 – 400 GHz
- Magnet: PPMS superconducting magnet (7T)
- Temperature: down to 2 K
- Source and Detector: Schottky diodes and Millimeter Vector Network Analyser (MVNA)

Cylindrical cavity chamber with 50.4 GHz as the fundamental mode.

Source → Waveguides → Cavity → Waveguides → Detector

Purpose: To observe the EPR signal from a Ho POM single crystal and to identify the orientation of the “easy-axis” of magnetization for the crystal

Analysis and Results

Figure 2. Angle dependent EPR spectra collected at 2K and 50.4 GHz. The data represent one of 9 end-plate positions (other positions not shown). The spectra show the expected 8 transitions as a result of hyperfine coupling.

Figure 3. Plot of absorption peak positions from figure 2, as a function of angle orientation.

Figure 4. This plot was obtained by collapsing the corresponding +m and -m transitions from the above plot to evaluate the g-value of the crystal.

Figure 5. Plot showing the peak positions at the minima for 9 end plate orientations.

The angle dependent data shown above correspond to position “5” for the end-plate and shows the “easy-axis” orientation.

The g-value for the Ho POM crystal was calculated to be 1.27

References and Acknowledgments


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Instrumentation

Zeeman Effect: E = hf = BμB

h = Planck’s constant
f = microwave frequency
B = magnetic field
μ = Bohr magneton constant
g = g-factor

Purpose: Sample: Holmium based polyoxometalate (POM)
- Anisotropic inorganic crystal consisting of a Lanthanide ion (Ho3+) encased in a non-magnetic ligand.
- Exhibits Single Molecule Magnet (SMM) properties
- Potential candidate for application in spintronics

Experiment

Electronic configuration: Ho3+= [Xe] 4f10
Nuclear spin: I = 7/2
- Unpaired 4f outer shell electrons exhibit the Zeeman effect in an applied magnetic field.
- Hyperfine coupling due to strong interactions between electron and nuclear spins is expected to cause EPR signal to split into (2I + 1)=8 peaks.

Figure 1. Schematic energy level splitting diagram showing expected transitions (blue arrows) for an electronic transition experiencing nuclear hyperfine coupling, with a nuclear spin of I = 7/2.

Figure 4. This plot was obtained by collapsing the corresponding +m and -m transitions from the above plot to evaluate the g-value of the crystal.

Conclusion

The angle dependent data shown above correspond to position “5” for the end-plate and shows the “easy-axis” orientation.

The g-value for the Ho POM crystal was calculated to be 1.27

Angle corresponding to end-plate position/degrees.