# Characterization of molecular magnets using EPR

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## I. Introduction

Molecules involving tetracyanoethylene (TCNE) and transition or rare earth compounds have been found to exhibit magnetic properties at low temperature. One compound, however, with V and TCNE has been found to have an ordering temperature above 300 K[1]. A compound with Fe and TCNE has shown to exhibit 32% more magnetization in molecules than iron metal. Molecular magnet compounds can be dissolved in a solvent, added to a matrix such as a polymer, and do not require metallurgical processing[2]. Since magnetism is a very basic science, application possibilities for molecular magnets are broad, stretching from nanotechnology to high density information storage[3].

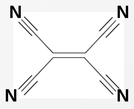



**Figure 1.** Chemical Structure of TCNE

## II. Theory

### a. About magnetism

Magnetism is reliant upon the ordering of spins or magnetic moments. Depending on the ordering of the spins, there can be three basic types of magnetism: para-, ferri-, and ferromagnetism[4].

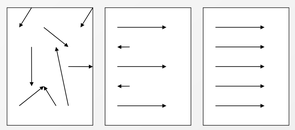


**Figure 2.**

*Paramagnetic*— no order: net magnetic moment =0

*Ferrimagnetic*— some order: net magnetic moment ≠ 0

*Ferromagnetic*— ordered: strong magnetic moment

### b. About EPR

Electron paramagnetic resonance (EPR) measures energy differences associated with the interactions of unpaired electron spins in the presence of an external magnetic field. An electron has a magnetic moment and aligns itself either parallel or anti-parallel to an external magnetic field. Absorbance occurs when the energy difference between these two situations is equal to the energy given by microwave radiation. The EPR system generates a constant microwave energy (ν ~9.5 GHz) and scans the magnetic field, yielding an absorption spectrum. The spectrometer plots the first derivative of the absorption curve[5].

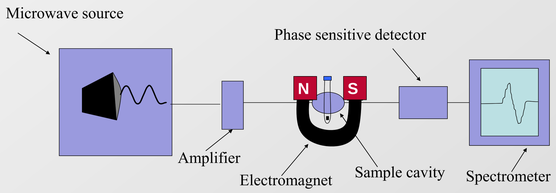
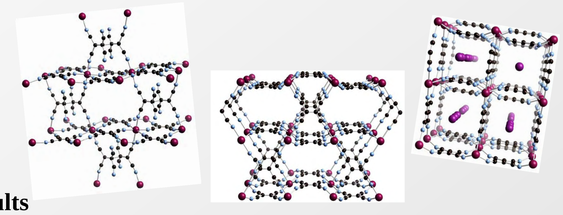



**Figure 3.** The diagram of an electron paramagnetic resonance system

## III. Experimental Procedure

- Two samples in ESR tubes were received from Dr. Joel Miller from University of Utah: **Mn[TCNE][$C_4(CN)_8$]$_{1/2}$** and **Mn(TCNE)$_{3/2}$I$_{3/2}$**. (Samples A and B).
- EPR spectra taken at 10-80 K for Sample A and from 10-260 K for Sample B, in 10 K intervals.
- Data integrated, then fitted to a Lorentzian and a Gaussian, for Samples A and B, respectively.
- Fitted functions integrated to obtain the intensity of each plot.



## IV. Results

The EPR curves were obtained at the specified temperatures. Two at ~20 K and 80 K have been chosen for comparison.

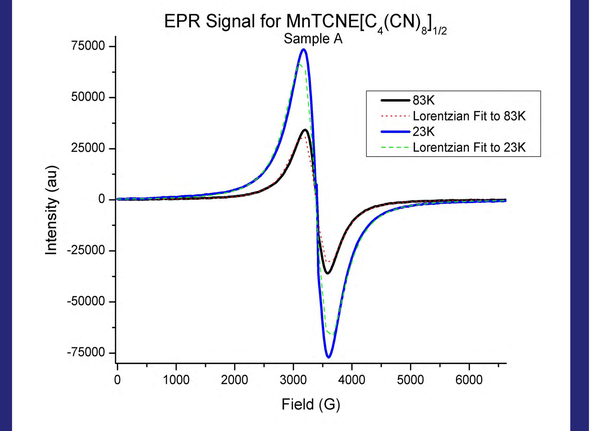



Figure 4. EPR lineshape for Sample A at 23 K and 83 K

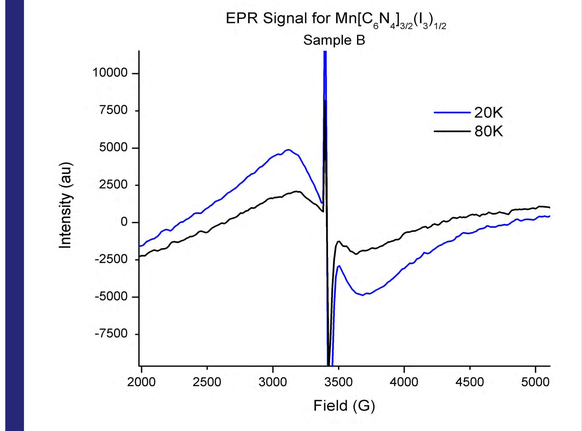



Figure 5. EPR lineshape for Sample B at 20 K and 80 K (Note: spikes are artifacts)

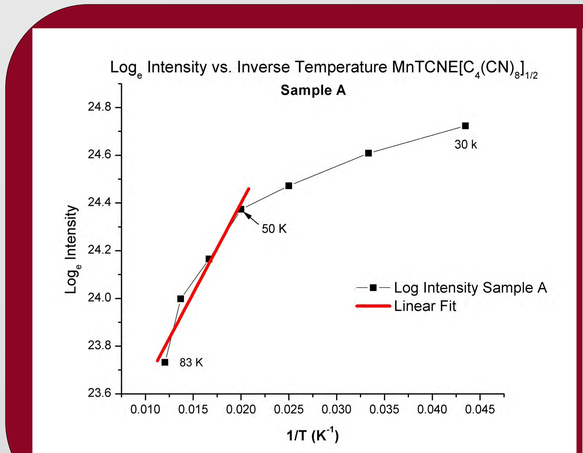



Figure 6. Logarithm of intensity versus inverse temperature from 30-83 K for Sample A

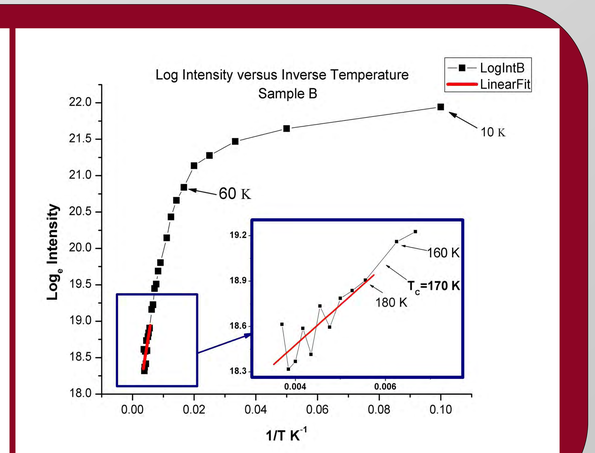



Figure 7. Logarithm of intensity versus inverse temperature from 10-260 K for Sample B

The natural log of the intensity versus inverse temperature was plotted to observe the ordering behavior of the material with respect to temperature.

## V. Discussion

From the data seen in Figures 4 and 5, intensity and temperature are inversely related. At lower temperatures, the relaxation time will be greater, thus the population of ordered spins will also be greater. The Lorentzian was used to fit the data for Sample A because the line width decreased as a function of temperature. But for Sample B, the line width changed slightly, so a Gaussian was a better model.

In large disordered systems of molecules or atoms, such as in Samples A and B, when in thermal equilibrium, Boltzmann statistics is applicable. The equation is an exponential[6]:

$$\textit{Boltzmann Factor} = A\, e^{-\Delta E/kT},$$

where $\Delta E$ is the energy difference between parallel/anti-parallel spin states, $k$ is the Boltzmann constant, and $T$ is temperature (K).

When the data is plotted as natural log of intensity versus 1/T, the Boltzmann characteristic should be visible as a straight line (see fitted lines in Fig. 6 and 7). At lower temperatures, the increased ordering of the spins causes there to be a diversion from the Boltzmann behavior. Where there is complete order in the system, the data should approach a horizontal line. However, in Sample B, there is a curved line, indicating a range of ordering temperatures instead of a specific temperature. In Sample A, the predominant ordering temperature, or Curie Temperature, was found, in research by Joel Miller, to be $T_C$ ~170 K.

## VI. Conclusions

- Sample A has a stronger paramagnetic response than Sample B by a factor of 5, which could be due to the presence of iodine in Sample B.
- There is an asymptotic ordering relationship as temperature decreases, meaning that both samples are ferrimagnetic at low T
- From our data, Sample B does not have a specific ordering temperature, but rather a distribution of ordering temperatures

## VII. Future Work

- Acquisition of fresh samples of A and B from Joel Miller
- EPR on Sample A and B full range from 10-300 K (A data was not broad enough, B data showed contaminant in equipment)
- EPR on Fe(TCNE)$_2$ from 10-300 K to find ordering temperature and study lineshapes according to temperature
- Crystal structure and relation to spin ordering to be studied in detail

## VIII. Acknowledgments

This work is supported by the National Science Foundation under Grant No. DMR-0820518 through the Renewable Energy Materials Research Science and Engineering Center (REMRSEC) REU program.

## IX. References

1. Plachy, R, Pokhodnya, K. I., Taylor, P.C., Shi, J., Miller, Joel S., and Epstein, A.J., Phys. Rev. B70, 064411 (2004).
2. Miller, Joel S., Epstein, Arthur J., Coord. Chem. Rev. 206-207 (2000) 652.
3. Epstein, Arthur J., Miller, Joel S., Syn. Met. 80 (1996) 231.
4. Askeland, Donald R., and Pradeep P. Fulay. *Essentials of Materials Science & Engineering*, London: Cengage Learning, 2010. p. 731.
5. Weil, John A., Bolton, James R., Wertz, John E. 1994. *Electron Paramagnetic Resonance*, New York: Wiley-Interscience pp. 7.
6. Schroeder, Daniel V. 2000. *An Introduction to Thermal Physics*, San Francisco: Addison-Wesley pp. 220.

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