

AC Susceptibility Measurements of the Spin Crossover Compounds

$[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ and $[\text{Fe}(\text{pz})\text{Pt}(\text{II})(\text{CN})_4] \cdot 2\text{H}_2\text{O}$

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Abstract

Spin crossover compounds are of significant interest to the scientific community because of their distinct magnetic properties. These compounds undergo phase transitions from low-spin to high-spin state and vice versa when exposed to certain stimuli, such as a change in temperature, pressure, or valence state by radiation. Specifically, this study is concerned with the characterization of the magnetic behavior of compounds $[\text{Fe}(\text{pz})\text{Pt}(\text{II})(\text{CN})_4] \cdot 2\text{H}_2\text{O}$ and $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ due to thermal variation. Both compounds exhibit spin crossover from low-spin to high-spin due to temperature increase. In $[\text{Fe}(\text{pz})\text{Pt}(\text{II})(\text{CN})_4] \cdot 2\text{H}_2\text{O}$ this crossover occurs around 240 K, whereas that in $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ occurs at about 350 K. Each compound shows hysteresis upon cooling and switches back to a low-spin state. The spin crossover for both compounds is accompanied by a dramatic thermochromic effect. Attempts using a tunnel diode oscillator (TDO) and mutual inductance coils were made to acquire magnetic susceptibility data on the spin crossover for $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ and a superconducting quantum interference device (SQUID) magnetometer was used for measurements on $[\text{Fe}(\text{pz})\text{Pt}(\text{II})(\text{CN})_4] \cdot 2\text{H}_2\text{O}$.

Introduction

The unique properties of spin-crossover iron(II) complexes have piqued the interest of physicists and chemists for decades. These compounds exhibit a phase transition induced by a variation in temperature, pressure, or valence state by radiation. [1,2]. This is characterized by a change of the electronic spin state, from low-spin to high-spin. Specifically, the electrons transfer from the t_{2g} to the e_g orbital, and switch spin state. The change in spin number is $\Delta S = 2$, where the low-spin $S = 0$ state is diamagnetic while the high-spin $S = 2$ state is paramagnetic [1, 3]. Magnetic susceptibility measurements of such compounds convey information on the spin states through the equation

$$\chi = \frac{\mu_B^2 N_A g^2}{3k_B T} S(S+1) \quad (1)$$

where χ is magnetic susceptibility, $N\mu_B^2/3k$ are all constants and equal to about 0.125 emu K/ mol, T is temperature in Kelvin, g depends on the molecular structure of the compound, and S is the spin quantum number. Multiplying χ by T, we obtain the value of the Curie constant, C, for a particular compound, since $\chi = C/T$ in abbreviated Curie Law form. A graph of χT vs T will merely be a horizontal line, unless there is a spin crossover at a particular temperature. However, complications arising from structural changes, magnetic interactions, and variations of g will also cause deviation in the Curie constant. In the case of spin crossover, an abrupt leap of the Curie constant is observed due to the change in S value or transition to high-spin state. The transition to the high-spin state occurs at a higher temperature than the low-spin transition. For example, if a compound is heated and transfers from low-spin to high-spin state at around 360 K and then cooled,

it may not go back to low spin until 300 K. Thus, a 60-K-wide hysteresis region can be observed. The bistable property of these compounds may lead to novel applications for sensor, display, and storage devices [3].

This study investigates the magnetic properties of the compounds $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$, hereafter **1**, and $[\text{Fe}(\text{pz})\text{Pt}(\text{II})(\text{CN})_4]\cdot 2\text{H}_2\text{O}$, referred to as **2**. Both materials exhibit a thermally induced spin phase transition with hysteresis and thermochromic effect. More specifically, the temperature of transfer to high-spin for **1** is about 350 K, and low-spin occurs around 320 K. The thermochromic effect associated with the phase transition is seen as a change of color from purple to white. However, after many cycles or extensive heating, the transition temperatures and hysteresis curve is shifted [4]. Similarly, **2** undergoes transition to high-spin at 240 K and to low-spin at 220 K; the color of the compound changes from a yellow to a garnet when transitioning to high-spin [2].

A superconducting quantum interference device (SQUID magnetometer) will be utilized to acquire magnetic data on **2**, but the transition temperature for **1** is beyond SQUID temperature range. So the majority of the experiment consists of creating and using alternate electronics and equipment, such as a small oven, to perform AC susceptibility measurements at higher than room temperatures.

Experiment

Two methods were used to measure the magnetic susceptibility of **1**. Initially, mutual inductance coils seemed like a simple way to perform AC susceptibility

measurement, but there are some disadvantages. Another method involves the use of a tunnel diode oscillator (TDO) circuit. First, the setup for AC susceptibility measurements is discussed for mutual induction coils. Then this method is analyzed for the information it conveys about the susceptibility of the compound. However, measurement with mutual induction coils did not come to fruition, and the TDO configuration was selected.

Mutual induction coil configuration

The mutual induction coil in our setup consists of a primary “excitation” coil, which resides inside a secondary “pick-up” coil. The secondary coil is comprised of two counterwound coils, such that if both sides of the secondary are empty, there is no output recorded on a lock-in amplifier. This arrangement allows only the magnetization of the sample, which is placed in one side of the secondary coil, to be detected. The experimental setup for the mutual induction coils is shown in Figure 1.

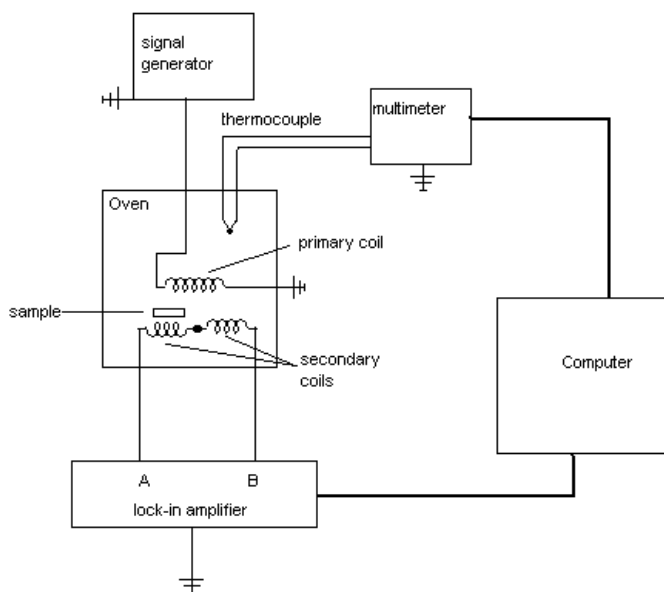


Figure 1. Mutual induction coil circuit

The primary coil receives excitation from the HP 3314A function generator. A sample of the material sits inside one end of the secondary coil. The secondary coil delivers its output to the A and B inputs on the EG&G 5302 lock-in amplifier. Both primary and secondary coils reside inside the Fisher Scientific laboratory oven. A copper/constantan thermocouple connected to a HP 3478A multimeter records the temperature inside the oven. The multimeter and lock-in amplifier are connected via GPIB cable to the computer. The computer is equipped with Labview software and an IEEE input/output card so that data acquisition is automated.

Mutual inductance measurement

Mutual inductance coils operate on the principle that a change in magnetic flux induces a voltage output. The primary coil is responsible for providing the AC magnetic field, while the flux of that changing field is detected by the secondary coil. The secondary coil experiences an induced current, and a voltage output can be recorded. This voltage output is proportional to the magnetization of a sample inside the secondary coil. The equation $M = \chi H$ relates this measured magnetization (M) to the magnetic susceptibility (χ) of the sample compound.

Although mutual induction seems like an easy way to acquire susceptibility data, the actual construction of the coils and balancing procedure hindered progress with this method. Since the compound under investigation emits only a tiny magnetic signal, the sensitivity of the coils needs to be maximized. Sensitivity of the coils is achieved by adding many layers of windings to both the primary and secondary coils, then increasing the excitation voltage to 10 V, the function generator maximum. The frequency of the

function generator is also tweaked to reduce noise and increase signal output. However, the addition of more coils and increased voltage incurs greater difficulty in the process of balancing the coil, which increases the risk of breaking leads off the coil and restarting the process. So, the TDO circuit method was introduced.

TDO experiment setup

The tunnel diode oscillator circuit is shown in figure 2. A voltage divider, which contains two batteries and two variable resistors, drives the tunnel diode and LC circuit. The sample is placed within the inductor, L, which resides in the oven. A capacitor C is connected in parallel with the inductor. This capacitor is due to the self-capacitance of the entire circuit, but still establishes the necessary LC oscillation. An rf amplifier (powered at 15 V) connected in series with a capacitor, $C_1 = 0.2 \text{ pF}$, is used to amplify the signal before being read by an HP 5385A frequency counter. The copper/constantan thermocouple connected to the HP 3478A multimeter records the temperature inside the oven. The computer and Labview are again used to record the data output from the frequency counter and multimeter.

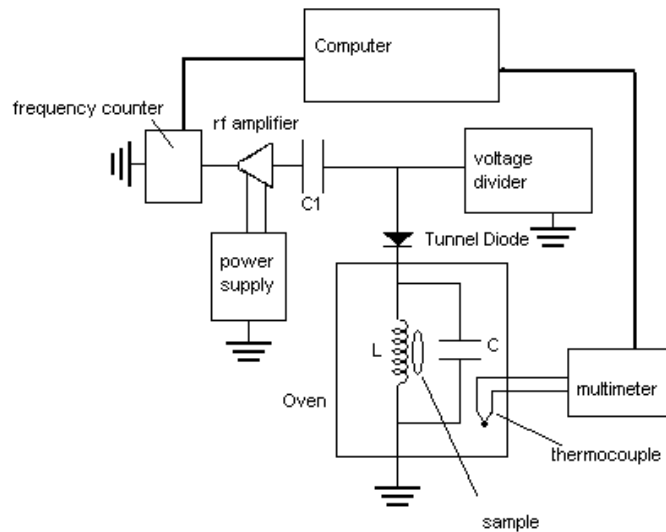


Figure 2. Tunnel Diode Oscillator circuit

TDO measurement

The tunnel diode oscillator operates when the tunnel diode is in the negative differential resistance state. The diode in its negative differential-resistance state along with the LC circuit maintains a steady oscillation. When a sample of some magnetization is set inside the inductor, the change in inductance is seen as a change of frequency. In LC circuits the frequency is related to inductance by $f = 1/2\pi(LC)^{1/2}$, where f is frequency, L is inductance, and C is capacitance. The equation $\Delta L/L_0 = \Delta f/f_0$ is the relation of the relative change of frequency from f_0 to the relative change of induction from L_0 . Since $L \sim (1+\chi)N^2A$, (where χ is susceptibility, N is the number of turns of the inductor, and A is the area of the inductor's core), the relative change in frequency $\Delta f/f_0$ conveys the magnetic susceptibility value.

Results

TDO

First, background (empty coil) measurements are performed to see the correlation of frequency to temperature change inside the oven. There should be a consistent dependence on temperature, with reproducible data from background sweep to background sweep. The background signal occurs because there is thermal expansion of the coils, which may change the capacitance, and an increase of resistivity of the wire. However, the background sweep may not be reproducible exactly, so it is more imperative to establish a dynamic range for the background and sample data. Once this is attained the sample data are recorded and the background subtracted. Then any remaining change in signal is from the sample itself.

Several background sweeps were performed; initially the data was not reproducible. However, after some adjustments and adding a capacitor in parallel with the tunnel diode to stabilize oscillations, two similar background sweeps were achieved. Figure 3 shows the two different sweeps with the same configuration. It is important to note the similar shape and range of the background data.

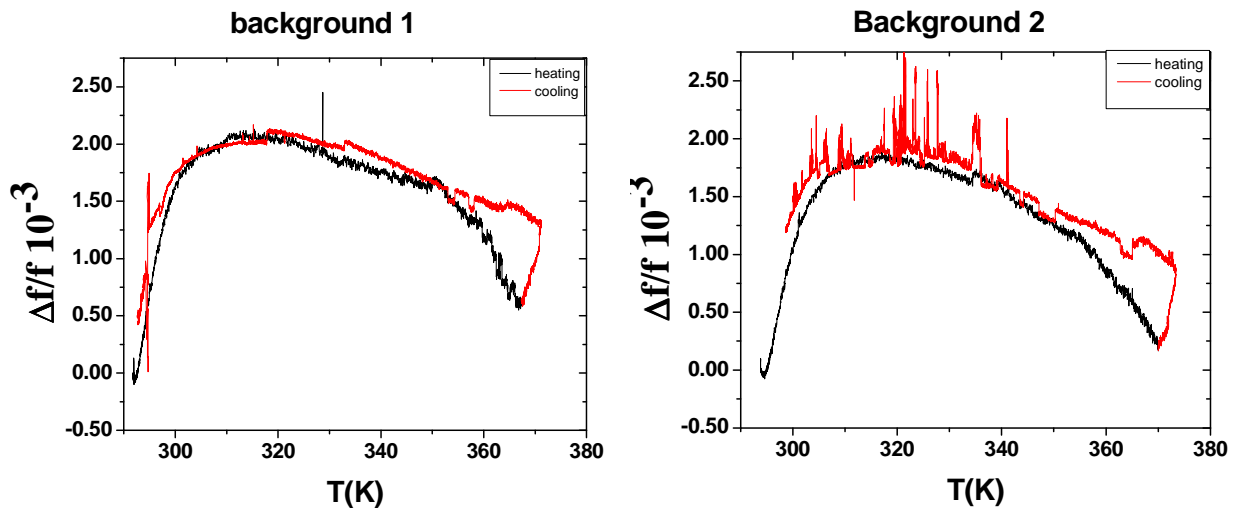


Figure 3. Oven background with the tunnel diode oscillator.

Since the signal in the low-spin state may not be in the dynamic range, the high-spin state could appear beyond the established range of background data. Since the background seemed reproducible, a sample run was performed. Figure 4 shows the data when the sample is inside the inductor. The sample data shows a distinct difference in amplitude and some difference in shape. There is a possibility of a crossover signal behind the background.

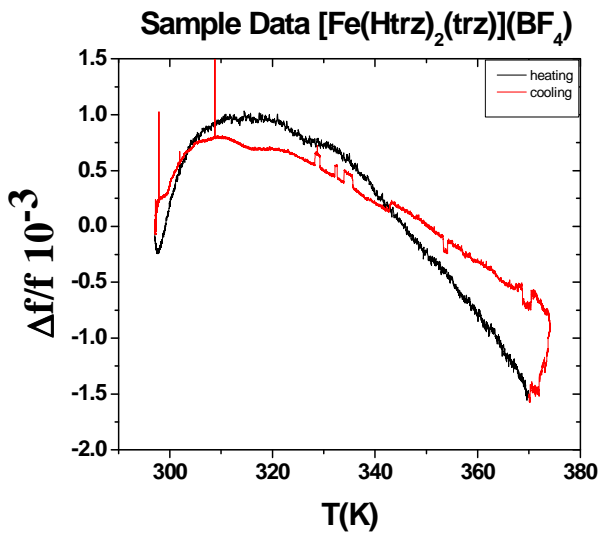


Figure 4. Sample plus oven background of tunnel diode oscillator circuit.

It now seems possible to extract the crossover signal by subtracting the background from the sample data. Figure 5 shows the subtraction of background from sample for only the heating mode. A signal that is characteristic of crossover from low-spin to high-spin occurs around 340 K. The cooling mode data is not as refined as the heating, so crossover signal could not be extracted.

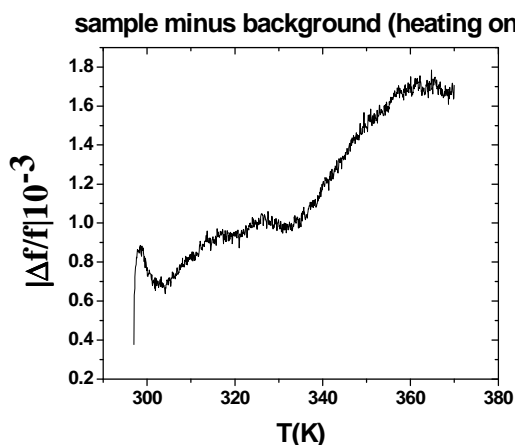


Figure 5. Background minus sample data for [Fe(Htrz)₂(trz)](BF₄) using a tunnel diode oscillator circuit.

SQUID

The SQUID measurements for $[\text{Fe}(\text{pz})\text{Pt}(\text{II})(\text{CN})_4]\cdot 2\text{H}_2\text{O}$ display transition to high-spin at 240 K (see Figure 6) and transitions to LS around 250 K. The χT value at room temperature is about 2.5 emu K/mol. This susceptibility at 300 K is different than the value reported in previous studies. Specifically, instead of a χT value of 2.5 emu K/mol, previous reports suggest the value to be around 3.2 -3.8 emu K/mol [2,3,5].

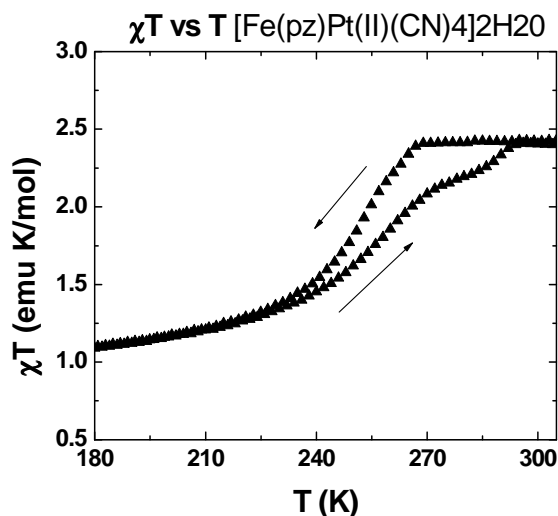


Figure 6. SQUID data for $[\text{Fe}(\text{pz})\text{Pt}(\text{II})(\text{CN})_4]\cdot 2\text{H}_2\text{O}$.

Several methods of measuring spin crossover have been studied. Mutual induction coils and TDO were used to perform AC susceptibility measurements at high temperatures for $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$. Although the mutual inductance coil method did not get beyond the construction phase of the experiment, the tunnel diode oscillator seemed to have produced results. Yet, these results are not entirely conclusive. There is a possibility that the process of inserting the sample into the coil, not the sample itself, changed the shape and values of the data curves, since the TDO is sensitive to even small movements and adjusting. So further tests and more data acquisition is necessary to confirm that the signal exhibits spin crossover. However, there is a more conclusive result associated with the thermochromic effect. As noted in the literature, the hysteresis

curve broadens as further cycles or extensive heating occurs [2-5]. This property was witnessed due to the thermochromic effect after heating the sample to 450 K for about 2 hours. The sample changed from purple to white, and remained white after cooling, albeit a few pink particles had transitioned. This phenomenon is evidence that the low-spin transition is shifted to a lower temperature than anticipated, and the hysteresis broadened.

The SQUID data for $[\text{Fe}(\text{pz})\text{Pt}(\text{II})(\text{CN})_4]\cdot 2\text{H}_2\text{O}$ shows a phase transition at temperatures that agree with the literature, but the value of susceptibility does not. The discrepancy may be due to some impurities found in the compound or to inaccuracies in the literature. However, we can perform a simple calculation to approximate g in eq (1), which will verify that the χT value at 300 K makes sense for the high-spin state. First, we know $\chi T = 2.4$ at 300 K, then assume $g = 2$, and solve for $S(S+1)$. Then we use this value for $S(S+1)$ to solve for g . Upon doing this, we find $g = 1.96$, which is in the range of acceptable values for g .

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