Characterization of the magnetic properties of Fe[(Htrz)$_2$(trz)](BF$_4$) using quartz tuning forks

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Abstract

The material, Fe[(Htrz)$_2$(trz)]BF$_4$, has been of special interest in the scientific community over the last few decades due to its unique spin transition properties near room temperature. Analysis of the magnetic properties of Fe[(Htrz)$_2$(trz)]BF$_4$ transpired from the use of quartz tuning forks commonly found in wrist watches. The resonant frequency and quality factor values were determined for each fork in the presence of zero magnetic field. The material was tested in two different magnets with field strengths ranging from 0 T to 1 T. Profiles of the magnetic fields were acquired by using a Toshiba Hall Sensor THS118. With a known magnetic field strength, the researchers compared resonant frequencies and quality factor values of the forks with and without Fe[(Htrz)$_2$(trz)]BF$_4$ nanoparticles attached. Data were also acquired from the material using a superconducting quantum interference device (SQUID) magnetometer. The magnetic susceptibility (χ) was then calculated along with the magnetic moment for the micrograms of Fe[(Htrz)$_2$(trz)]BF$_4$ placed on the fork.

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Introduction

Spin is an intrinsic property of all electrons, usually equated to angular momentum. An electron can be in one of two spin states: up or down. The magnetic properties of matter are determined by these spin states. Electrons orbiting molecular nuclei must be aligned in the same direction for a material to be magnetic. The alignment of electron spins produces an overall spin for the molecule. Molecules must then align with other molecules in the substance to produce a magnetic effect. Groups of molecules form domains. The total magnetic spin of the domains must line up with each other in order for a material to be magnetic [1]. Solids have the best chance at being magnetic because of their rigid structure of molecules. The molecules in most liquids and gasses have too much freedom of motion and rarely remain aligned.

Spin transition compounds, discovered about fifty years ago, have provided a new area of chemistry/physics exploration, especially in the past two decades. These compounds possess the unique quality of occupying a low spin or a high spin state depending on variations of temperature or pressure [2,3]. The resulting microscopic spin of the particles provides the macroscopic magnetic properties of the material, which can be diamagnetic, paramagnetic, or ferromagnetic. These properties can be incorporated into new devices such as switches and sensors.

Spin crossover compounds containing iron(II) are of special interest to the science community because these compounds exhibit spin transitions induced by the irradiation of light. Unfortunately, this reaction only occurs at temperatures below 50 K, posing a serious problem to the practical applications of this material [4, 5]. We researched $Fe[(Htrz)_2(trz)]BF_4$. The magnetic effects are associated with the iron atoms concentrated in the center of the structure as seen in Figure 1. After some adjusting using chemical methods, the spin transition of iron(II)
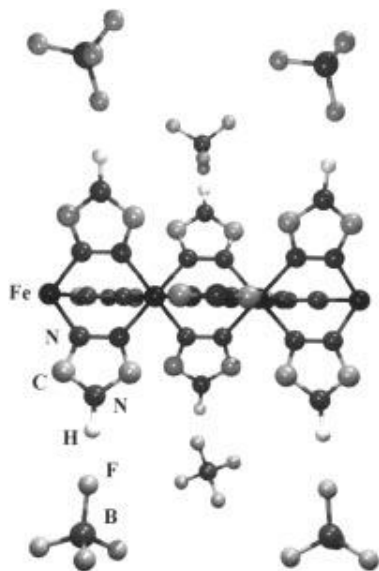
compounds can be shifted close to room temperature. A thermochromic effect is seen when the transition from low to high spin occurs. The material changes color from purple to white. Regrettably, after many cycles and/or excessively heating the sample a shift is observed at the transition temperature and hysteresis curve [2].

Experiment

In our experiment, the set-up is designed to test the spin transition material on quartz tuning forks [7] at their resonant frequencies. A clean tuning fork will be passed through a magnet while taking data on the amplitude of the fork's vibration at millimeter intervals. These data will provide a base to compare the forks with the material on them. A frequency generator (Agilent 33220A) drove the fork while a lock-in amplifier (Stanford Research Systems SR530) was utilized to record the amplitude of the oscillations (Figure 2). At the resonant frequency, the amplitude suddenly increases projecting a sharp peak onto the graphing program connected to the amplifier. After fitting the graph to a Lorentzian curve, we determined the exact resonant frequency (f_0), along with the full-width-half-maximum (Δf). The full-width-half-maximum is a measure of the width of the resonant peak at the value equal to one half of

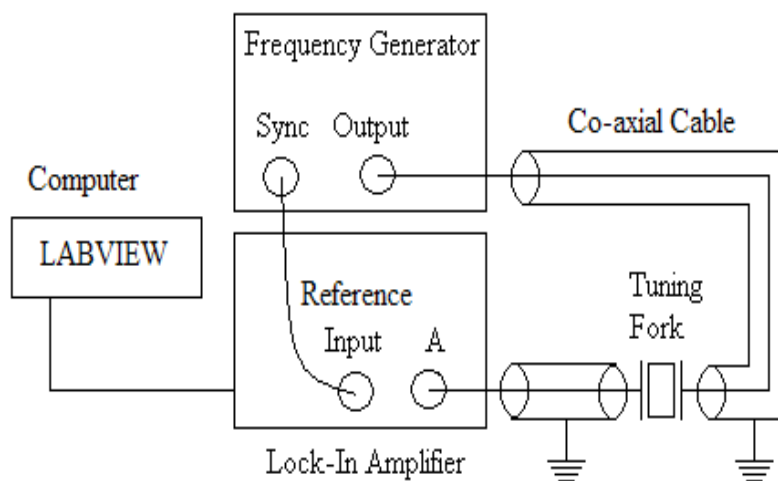Figure 1: (taken from [6]): Molecular structure of Fe[(Htrz)2(trz)]BF4.

Figure 2: Circuit diagram for measuring tuning fork resonance.

the amplitude of the resonant frequency. We then determined the quality factor (Q) of the tuning fork ($f_0 / \Delta f$). The quality factor is the ratio of the reactance to the resistance of an electric circuit. A high Q value describes a circuit where energy is dissipated slowly, while a low Q valued circuit loses energy rapidly. When purchased, the tuning forks are enclosed in a canister containing a very low pressure. This pressure value produces a very high Q value for the forks. Once removed the Q value decreases and the resonant frequency is also shifted, as depicted in Figure 3, meaning that a loss in signal resolution occurs when opening the forks. The loss of resolution could be caused by the fact that the pressure in the can is much lower than the atmospheric pressure outside the can. The resolution could also decrease in the process of opening the fork. In order to open the canisters we used a pair of diagonal pliers. The pliers were used to gently break the seal holding the can to the base of the fork. This procedure required some force and very well could have damaged the forks. The application of particles in nail polish also contributed to the decreased resolution. The change in resolution could also have arisen from a combination of these reasons.

The magnetic field was found by using a Toshiba Hall Sensor THS118 to record field strength at different points along the axis. The Hall sensor operates maximally when a current of 5 mA is passed
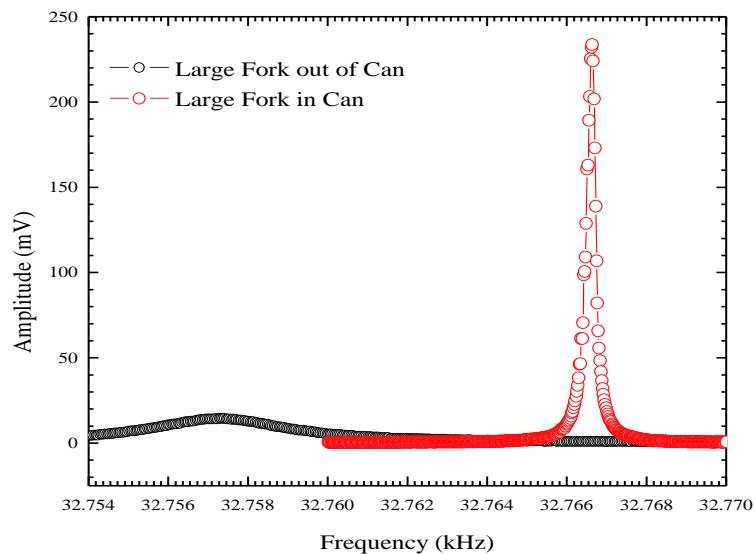

Figure 3: Resonance peaks for an opened and unopened fork.

4

through it. In order to achieve this scenario, the sensor was connected in series with a resistor of know resistance (2 kΩ). A variable power supply drove the circuit, with digital multi-meters measuring the voltage across the two elements. Applying Ohm's Law permitted the calculation of the current (Figure 4).   A voltage of 12.7 V powered the circuit with a 5 mA current. With a known Hall voltage the magnetic field strength could be calculated at each point, forming a profile of the magnetic field. Knowing the field profile allows comparison of field strength to any change/shift in the resonant amplitude. The material was tested in a 0.3 T magnet and a 1 T superconducting magnet (Oxford Teslat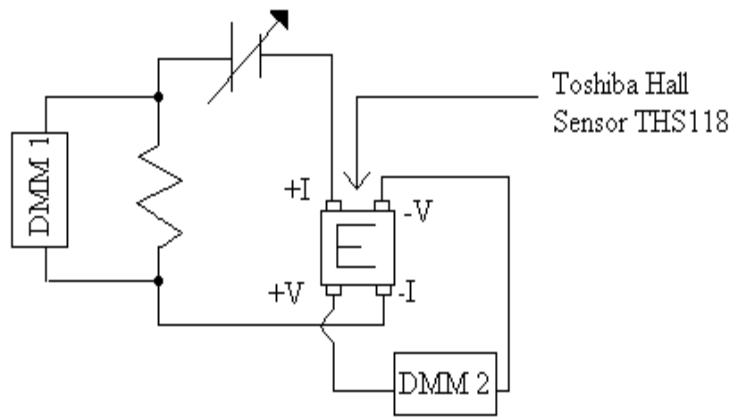ron) at room temperature   (Figure 5). The material was also analyzed with a superconducting quantum interference device (SQUID) magnetometer. The SQUID acquires data utilizing small magnetic fields at a range of temperatures (Figure 6).

Data

The tuning forks were then

Figure 4: Circuit diagram for the Hall sensor.

Outside
Magnet

Inside Magnet

Figure 5a:
Field strength as a function of
distance for the 0.3 T magnet.

5

Figure 5b:
Field strength as a function of
distance for the 1 T magnet.

loaded with Fe[(Htrz)$_2$(trz)]BF$_4$

nanoparticles. The particles were used in solution with clear nail polish (Sally Hanson: Hard as Nails). A needle was dipped into the well mixed solution and then used to apply a small amount of substance to each prong of the fork individually.
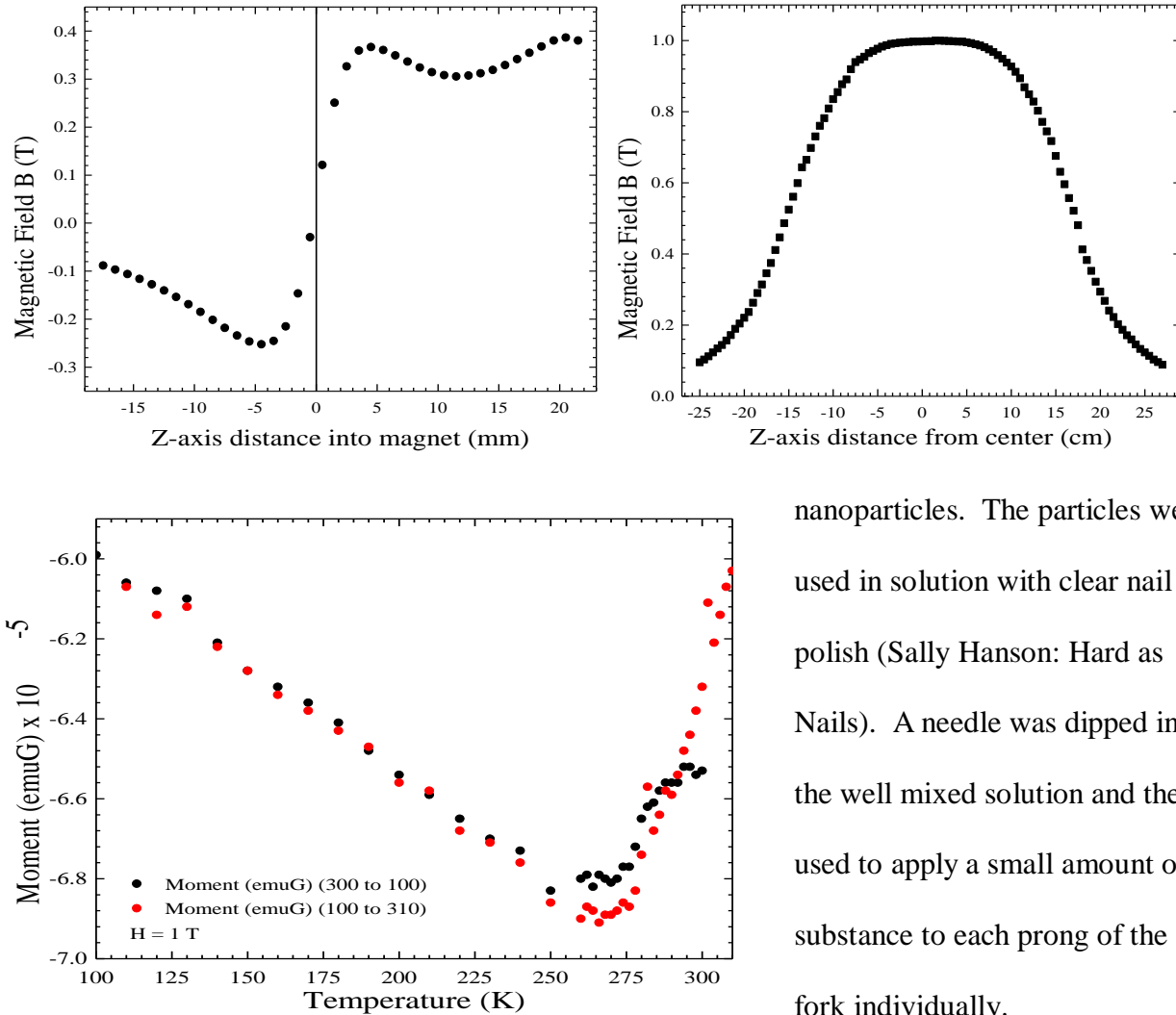
The fork was left to dry

Figure 6: Magnetic moment as a function of temperature for Fe[(Htrz)$_2$(trz)]BF$_4$ taken in a Quantum Design MPMSXL SQUID magnetometer in a 1 T field.

overnight. Once the fork was loaded with nanoparticles, the fork was placed in the same circuit

and run through both magnets. The frequency and amplitude were again measured at different

magnetic field strengths. The runs were graphed in a waterfall style to see if the resonant

frequency shifted at all as observed in Figure 7. A graph of a clean fork would have all resonant

frequencies equal, along with equal amplitudes. The particles did not really shift the resonant
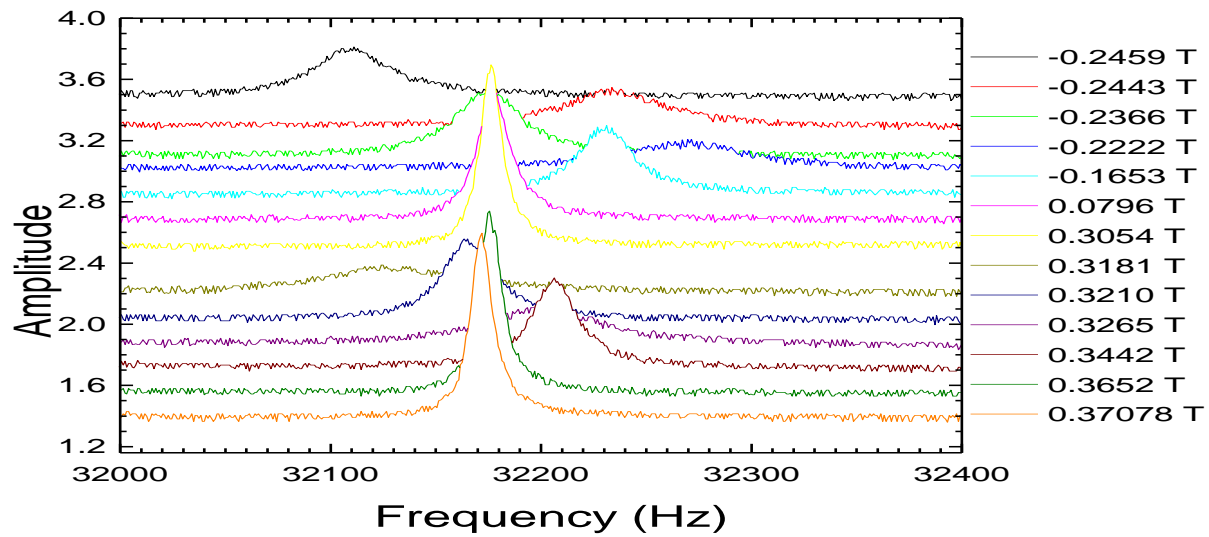
frequency as much as we had hoped. However, the Q values varied greatly. The magnetic force

on the particles must have affected the fork in order to explain this variation.

Results

The next step was to analyze whether or not the Q values changed and whether or not any

hysteretic behavior was observed from the fork. Fitting and graphing the frequencies and Q

values against field strength was where we hoped to see results (Figure 8a). Unfortunately, the

data did not show a hysteresis loop in the 0.3 T magnet. The gradient may have also been

responsible for providing the force on the particles that caused the frequency shifts. Similarly to

the magnetic field strength, the graphs of resonant frequency and Q against B*(dB/dZ) did not

clearly show a hysteresis loop (Figure 8b). While taking data we observed major interference
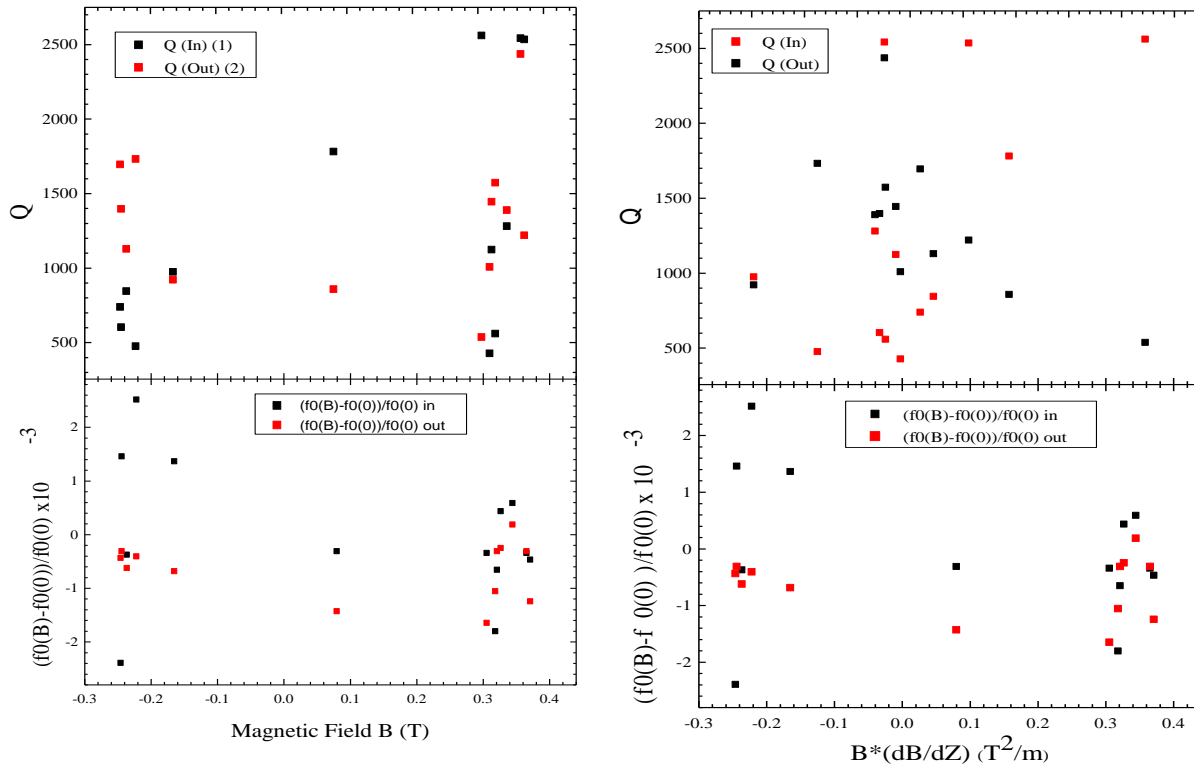
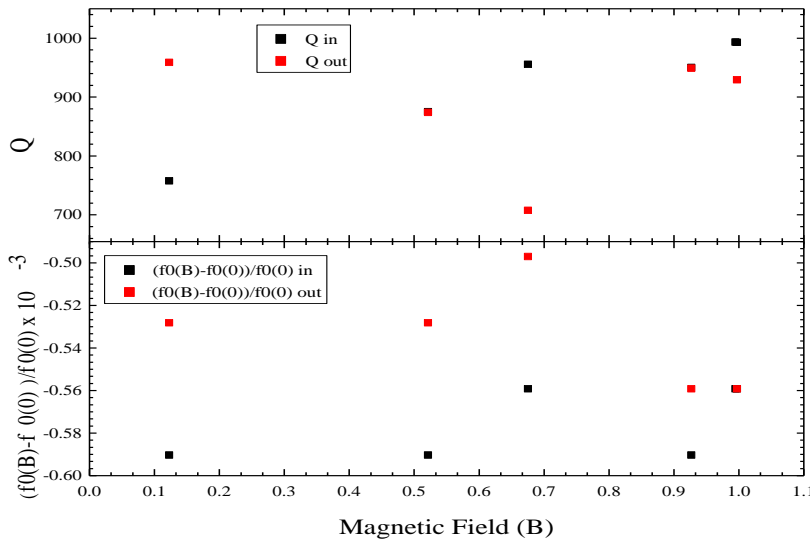from the environment. The scatter in the data caused by the noise from the lab may well have

affected the data to a degree. We then moved to the 1 T magnet and preformed the same analysis (Figures 9a and 9b). Since the 1 T magnet has an enclosed coil, some of the environmental noise
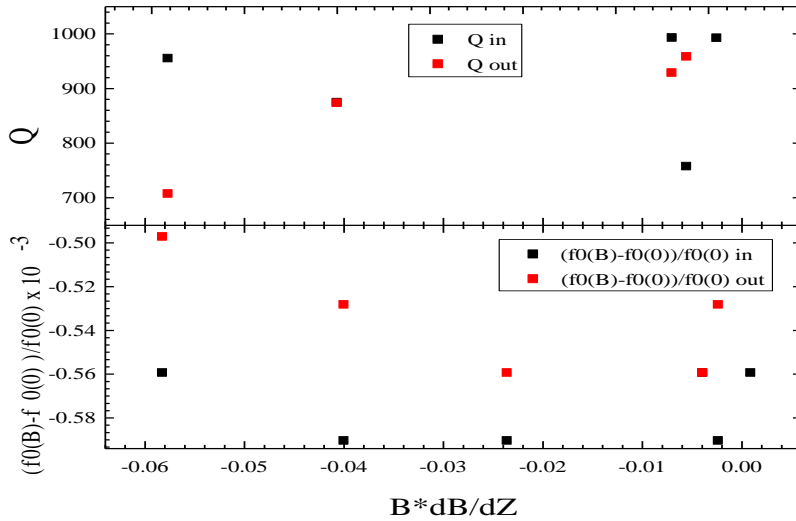
Figure 9a: Resonant frequency in field divided by resonant frequency with no field as a function of magnetic field strength. Quality factor as a function of field strength. Both taken in the 1 T magnet.

Figure 9b: Resonant frequency in field divided by resonant frequency with no field as a function of B*(dB/dZ). Quality factor as a function of B*(dB/dZ). Both taken in the 1 T magnet.

was filtered out. As expected, Q values decreased in the stronger magnetic field. There seems to be a stronger correlation between the data in the 1 T magnet as opposed to the smaller 0.3 T magnet. However, the data appear to form a flat band when accounting for the uncertainty. In order for the data to be acquired, we had to extend the wire connections to almost three feet in length. The lengthening of the wires added more capacitance to the circuit, further affecting the Q values.

Our next conclusions are to be drawn from the magnetic susceptibility (χ) of the material. This value, equal to the magnet moment divided by magnetic field strength, provided important information regarding the reliability of our experiment. The magnetization of the nanoparticles is about -1.5×10^{-3} emuG/g (derived from figure 6). The change in magnetization of the nanoparticles on the fork is about -1×10^{-2} emuG/g (derived from figure 8a). These data yield a signal to noise ratio of approximately 0.15. The magnitude of signal we receive from the lock-in amplifier is 15% of the magnitude of the noise received from the environment. We will not be able to conclusively see the affect of the magnetic fields on the $Fe[(Htrz)_2(trz)]BF_4$ nanoparticles with our current set-up.

Further research which can be done in this field will need to place a loaded fork in the same magnetic field, but at a different temperature. We want to see what effects if any occur if

9

the sample is in a different spin state. We need to devise a system for taking data from the fork while it is in a dry ice bath. The ice will bring the temperature of the set up down to slightly below 200 K, far below the transition temperature of nominally 275 K. A thermal couple will also have to be included in this next set up in order to measure the exact temperature, making sure the sample is in the low spin state. Another possible area to explore is the introduction of an operational amplifier into the circuit. The operational amplifier will enlarge the signal coming from the nanoparticles, which will increase the signal to noise ratio allowing more definite conclusions to be drawn.

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