

# Magnetic susceptibility studies of heterostructures of Prussian blue analogs

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## ABSTRACT

The goal of the experimental project is to repair and operate a closed cycle helium displacer to be used to measure the temperature dependence of the AC magnetic susceptibility of RbNiCr with RbCoFe Prussian blue analogs. Since the ferromagnetic transition temperature is expected in the range of 60-70 K, a closed cycle helium displacer will be used to generate the low temperature environment. The magnetic transition will be detected by a set of mutual inductance coils that provide a measurable voltage due to the magnetic signal of the sample. The reason for this project is to learn more about these structures and what characterizes them. Due to complications with the equipment it was not possible to measure the heterostructure in the displacer, but the bulk sample, RbNiCr powder, was measured in the commercial SQUID (Superconducting Quantum Interference Device) magnetometer, where the desired transition was seen around 70 K. The magnetic susceptibility measurement is important because it is a step towards distinguishing unknown properties of this new material and may one day lead to new technology.

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## INTRODUCTION

Susceptibility comes in two forms: electric and magnetic. Magnetic susceptibility is the ratio of magnetization to the magnetic field strength:  $\chi_m = \mathbf{M}/\mathbf{H}$  [1]. Alternating-current (AC) magnetic susceptibility is an important quantity in characterizing numerous materials such as heterostructures. AC susceptibility is frequency dependent, because it is measured using mutual inductance coils. The mutual inductance coils create and pick up the magnetic field of the sample structure through the changing voltage due to varying temperature. As the magnetic field increases there is an increase in inductance and a decrease in frequency shown by the resonant frequency of an RLC circuit:  $\omega = 1/\sqrt{LC}$ .

The reason for this experiment is solely “curiosity driven”. As new materials are explored more knowledge is gained about their properties and what characterizes them. The specific heterostructure being studied is ten layers of Nickel Chromium (NiCr), ten layers of Cobalt Iron (CoFe), and another ten layers of NiCr. Each material has a different critical temperature ( $T_C$ ) and different properties. NiCr is a ferromagnet meaning all the magnetic moments are aligned in the same direction giving rise to a magnetic field [2] and has a  $T_C$  around 90 K [4]. CoFe is diamagnetic meaning the material develops a magnetic moment opposite to any field [2] and displays antiferromagnetic magnetism around 20 K [4]. The purpose of this experimental project is to measure AC magnetic susceptibility of heterostructures of Prussian blue analogs in response to temperature. The goal is to see a magnetization transition of the material around 70 K; however, because this heterostructure has never been studied previously, the hypothesized outcome is not guaranteed. Testing the heterostructure at temperatures lower than liquid nitrogen is the first step towards creating new technology with this type of sample structure.

## CLOSED CYCLE HELIUM DISPLEX

A closed cycle helium displex consists of three main pieces of equipment: a compressor, an expander, also known as the refrigerator, and a diffusion pump. Figure 1 is a photograph of the experimental setup in the laboratory.

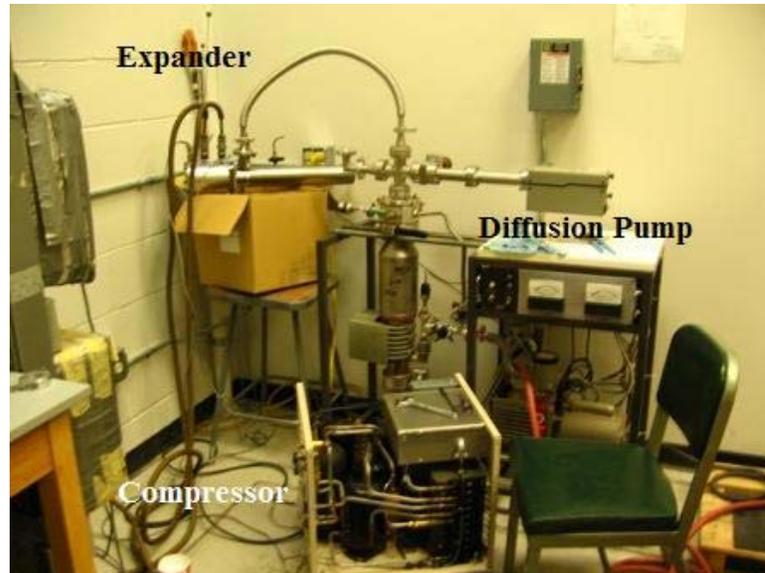


Figure 1: Closed cycle helium displex setup.

A compressor continuously extracts room temperature low pressure helium gas from a system return line. The helium is compressed, thereby changing it to cold high pressure helium gas, which is sent into the expander.

The refrigerator uses the Gifford-McMahon refrigeration cycle [3] (Appendix 1) to cool the helium to an even lower temperature and is supplied into the two heat stations. Figure 2 below labels the parts of the expander [6].

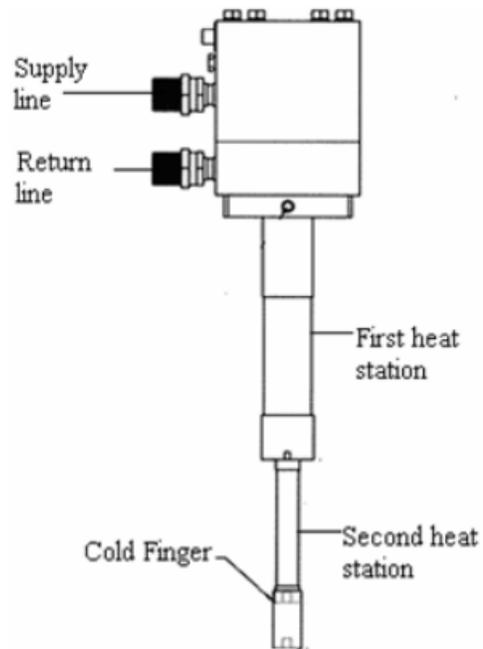


Figure 2: Parts of the expander.

The heat sink to which the sample and thermometry are mounted is located on the end of the second heat station, also known as the cold finger. The helium that is chilled by the compressor and the expander is blown through the heat sink, where the sample structure is located, to cool it to below nitrogen temperatures. Low pressure helium gas is returned through a system supply line back into the compressor. A vacuum can was machined to separate the sample from the room environment and to help maintain the high vacuum environment supplied by the diffusion pump.

The diffusion pump supplies the high vacuum environment needed to conduct the experiment. The diffusion pump works by using a high-speed jet of vapor to direct residual gas molecules in the pump throat into the bottom of the pump and out the exhaust [5]. The high-speed jet is generated by boiling low vapor pressure oil and directing the vapor through a

multistage jet assembly [5]. To ensure the correct pressure is reached a mechanical pump is used to back the diffusion pump. The specific labels for these pieces of equipment are an Air Products compressor module, model 1R02A, an Advanced Research System expander model DE 2-202, and a BOC Edwards E02K diffusion pump. A vacuum can was machined to encapsulate both heat stations, to separate the sample from the room environment, and to help maintain the high vacuum environment supplied by the diffusion pump.

Three different apparatuses are also attached to the cold finger in order to complete the experiment: a tunnel diode oscillator (TDO), a four wire resistance thermometer, and a chromel-gold iron (Chromel-AuFe) thermocouple. Figure 3 shows the schematic of how each instrument is attached to the displax and the controlling electronics.

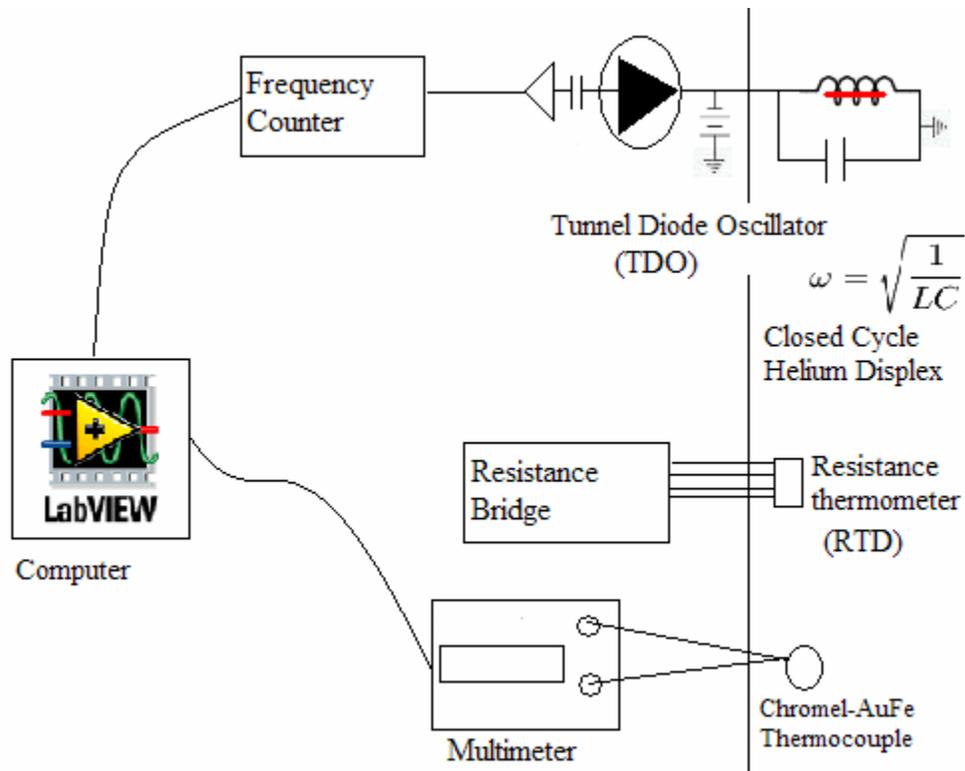


Figure 3: Schematic for Displex.

Instead of using mutual inductance coils to measure the change in the magnetic transitions a TDO was utilized. A TDO is a heavily doped p-n junction, which combines a tunneling current with a regular diode [8]. The TDO establishes a resonant frequency of a tank circuit (i.e. inductor, capacitor). The sample structure is located within the inductor of this circuit. A TDO consists of an inductor (i.e. a coil), and a Germanium Devices model BD-5 diode. A change in the temperature causes a change in the inductance, which results in an alteration in the frequency.

The four wire resistance thermometer (RTD) requires a small power source to measure the changing resistances and current. The resistances are measured with a resistance bridge and are compared to a certain temperature, which is determined through a known calibration.

The Chromel-AuFe thermocouple measures voltage versus time. The voltages can be correlated to specific temperatures. This was completed by calibrating against a known thermocouple in the laboratory, which resulted in this equation:  $-5.8132 + 0.01932x + (-0.0001x^2) + (1.1345 \times 10^{-6})x^3 + (-4.5634 \times 10^{-9})x^4 + (6.2427 \times 10^{-12})x^5$ .

Using a computer equipped with LabView software and an IEEE input/output cord, the temperature plot from the thermocouple, and the frequency plot from the TDO versus time is recorded.

Also a commercial SQUID was used to measure bulk sample. A SQUID magnetometer characterizes new materials by applying a magnetic field that can be varied over a wide temperature range [9]. The SQUID magnetometer consists of a superconducting magnet, superconducting pick up coils, a SQUID connected to the pick up coils, and a superconducting magnetic shield. As the flux changes through the superconducting pick up coils the magnetic moments of the sample change and are recorded as a change in voltage. Those voltages are plotted against position. Figure 4 below shows a cross-sectional picture [9] and an actual picture of a SQUID magnetometer.

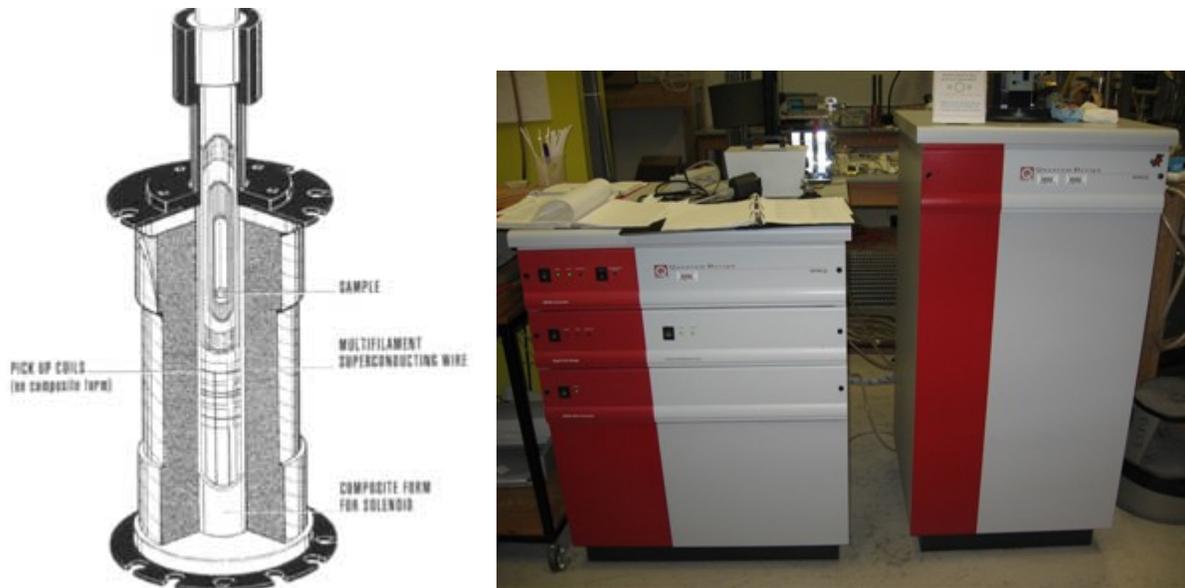


Figure 4: Cross-sectional SQUID picture and actual SQUID photo.

## EMPLOYING THE EQUIPMENT

Before a test run could be employed it was necessary to repair the thermocouple, because voltage could not be measure without it. There were a couple of ideas when it came to repairing the thermocouple. First, buy a new thermocouple. This idea was immediately discarded because of pricing. Second, use a different type of thermocouple, however, this idea was inconclusive because no other thermocouple reaches the temperatures needed. Lastly, keep the old thermocouple and repair it with the assistance of the machine shop. The last idea was more economical, easier and employed. The thermocouple took several tries to fix, but was finally accomplished. The compressor connects to the refrigerator through two braided flex hoses: one supply and one return. The diffusion pump connects to the refrigerator through one stainless steel tube, a quick connect flange, and a quick coupling. Figure 5 below displays the hose connections to the displer, compressor and the vacuum pumps.

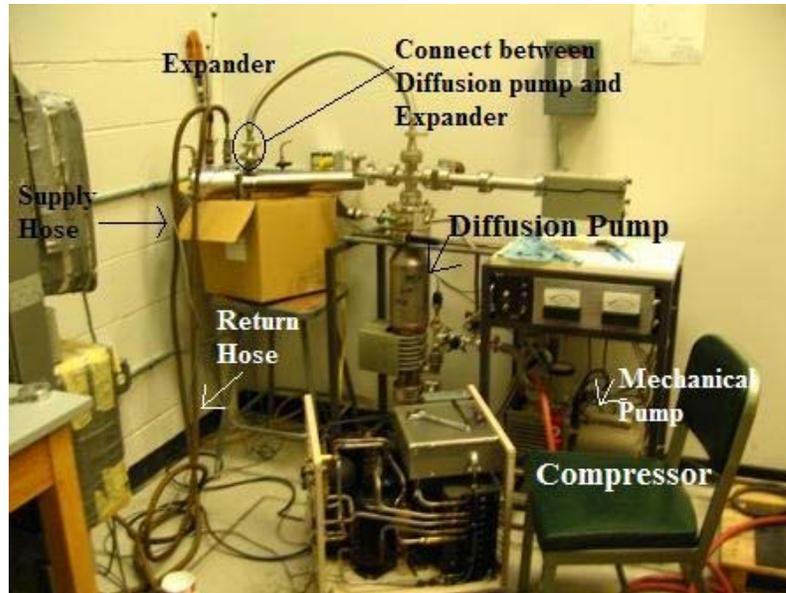


Figure 5: Labeling of complete setup.

An initial cool down run was completed to ensure the working ability of the compressor and the expander. For the first run only the mechanical pump was used instead of both the mechanical and diffusion pump. The primary test run used a screw as the test sample to be cooled. The displacer achieved a temperature of 59 K. Another cool down was fulfilled with both pumps. During the run, a leak was evident in the setup due to the hissing noise coming from the compressor. The location was found to be the hoses. Even though this leak was quite evident the displacer continued to cool down. The temperature attained by the displacer was 29 K, which is much lower than the transition temperature of the sample material and structure. The next step in the project was to add the TDO, the RTD, and LabView, purchase new hoses, and measure the bulk and actual sample.

Once the TDO and RTD were varnished and secured onto the cold finger of the refrigerator, the new hoses were attached to the compressor and displacer. The TDO and thermocouple were then connected to the computer through LabView software and an IEEE input/output cord to record temperature and frequency with respect to time. The RTD was

connected to a resistance bridge to measure the fluctuating resistances, which correlate to specific temperatures. At this point with all the instruments mounted to the cold head a cool down was to be run without and with the sample.

## DISCUSSION

The result I wish to obtain is a full functioning closed cycle helium displacer and a magnetic transition in the range of 60-70 K. From previous work on bulk material a ferromagnetic transition is expected. Due to the short supply of time and mechanical difficulties, I was unable to measure the heterostructure in the displacer, but I did measure the bulk material, an RbNiCr powder, in the SQUID. Figure 6 below presents the ferromagnetic transition as the temperature decreases.

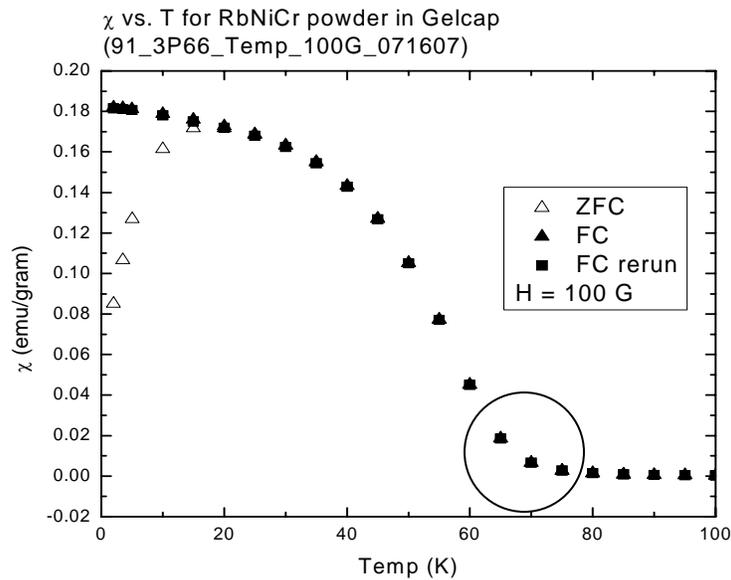


Figure 6: Susceptibility vs. Temperature.

The clear triangles are the warming data in a magnetic field of 100 G. The dark triangles are the cooling data of the sample powder in 100 G. Within the circle is the hypothesized ferromagnetic transition. The dark squares are a rerun of the dark triangles.

This measurement is important because it affirms the presence of a magnetic transition in the region of 60-70 K. Since new technology begins at temperatures lower than 77 K it is now possible to work towards measurements around room temperature. It may be possible with this transition new devices may be made.

Many problems occurred with the displex while trying to measure the bulk sample and heterostructure. The first problems were the broken thermocouple and leaky hoses, yet these problems were easily fixed. Once everything was connected onto the 1<sup>st</sup> and 2<sup>nd</sup> heat stations, more problems occurred. The TDO was not oscillating correctly and the thermocouple broke once again. A new problem also took place, the thermometer experienced a crack. I fixed the thermocouple; however, I was not able to fix the thermometer. After tinkering with the TDO, Dan Pajerowski, the graduate assistant, finally got it to oscillate. Consequently, I could not get each element to work together in the displex, but I could get most of them working separately. A second run was not accomplished due to the end of my stay here; however, Dan Pajerowski finally managed to get the displex working and it cooled to 13 K.

Because I was unable to measure the actual heterostructure sample in the displex, there are many logical next steps for this experiment. The first step is to get the RTD fixed and mounted on the cold finger. The second step is to maintain a constant oscillation from the TDO. The third step is to mount each piece of equipment back onto the displex and make sure it all works simultaneously, which allows for a full functioning displex. Once the closed cycle helium displex is fully functioning a measurement should be taken of the RbNiCr and the actual

heterostructure. Another step is to X-ray the sample to see if the structure is chemically bonded together instead of physics stacked together. The final step is to gradually increase the temperature until room temperature and make measurements with the displax on either sample.

## **ACKNOWLEDGMENTS**

I would like to thank Professor Meisel for advising me on this project. I would like to thank Dan Pajerowski, graduate student, and Justin Cohen, undergraduate student, with their assistance through out my project. I would like to extend thanks to the Talham Lab in Chemistry for letting me tinker with their displax for the summer. I would like to thank Mr. Bill Malfurs for his expertise in machining. I would like to thank National High Magnetic Field Laboratory and Professor Ingersent for giving me the opportunity to do summer research. I would also like to thank NSF for funding this program and University of Florida Physics Department for hosting me.

## **APPENDIX 1**

The Gifford-McMahon refrigeration cycle has no work transferred from the system because the displacer moves the gas from one expansion space to another. The process is described in Figure 7 below [7].

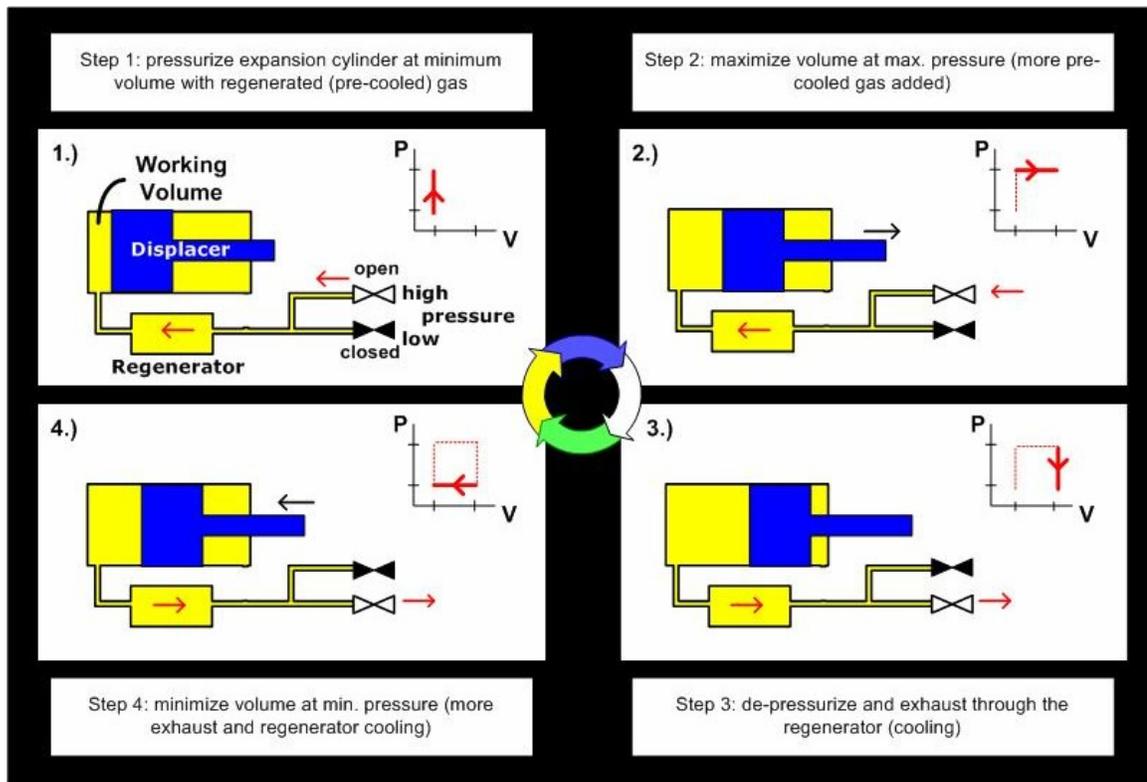


Figure 7: Gifford-McMahon Refrigeration Cycle.

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[9]

[http://www.nanomagnetism.org/instrumentation\\_and\\_characterization/squid\\_magnetometers.php](http://www.nanomagnetism.org/instrumentation_and_characterization/squid_magnetometers.php)