Phase Transitions in $CaFe_2As_2$ and $CeCoIn_5$ Under Uniaxial Pressure

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(Dated: September 12, 2009)

The sample $CaFe_2As_2$ was prepared for resistivity and susceptibility measurements under uniaxial pressure to investigate the suppression of a structural transition and the resulting emergent superconducting regime. Additionally, the sample $CeCoIn_5$ was prepared for susceptibility measurements to look at the change in T_c of a superconducting regime related to uniaxial pressure applied on the a-axis. The T_c of the superconducting transition in the $CeCoIn_5$ appeared to increase about 60 mK with a pressure increase of 2 kbars, which matches predictions made by thermal expansion. However, these results need to be confirmed because of exceptionally noisy data and the fact that the sample disintegrated during testing. Promising progress was also made on the $CaFe_2As_2$ samples, but the data for the superconducting dome is yet to be fully analyzed and data is still lacking to characterize the structural transition.

I. INTRODUCTION

As interest in high-T_c superconductors continues to increase, so does the necessity of understanding the mechanisms behind these and other highly correlated electron systems. If a material which is superconducting at room temperature and ambient pressure can be found, many applications of this amazing technology and its derivatives will prove exceptionally useful. One of the most useful properties of high-T_c superconductors is the ability transmit power with virtually no loss due to resistance. This application alone could be used in a plethora of areas including travel, industrial, residential, and commercial power usage, as well as computing.

To aid in the search for this room temperature superconductor, it is useful to examine materials similar to the high-T_c cuprates (copper-oxides). In this case the materials of choice are $CaFe_2As_2$ and $CeCoIn_5$. Both of these substances exhibit many properties which are strikingly similar to those found in cuprates, despite the fact that they have much lower superconducting transition temperatures, as well as other unique properties. One advantage to studying these low temperature superconductors is that at low temperatures, it is possible to discern patterns and properties that could be covered up by thermal activity at higher temperatures which have similarities to the high-T_c cuprates [2]. These materials have various structural and magnetic transitions which can be tuned by both doping and oxygen depletion [2] and when they are suppressed, a superconducting transition emerges, which can also be tuned using the same processes. While these techniques do allow changes in properties of the compound, it changes many parameters of the substance in often uncontrollable ways [1].

A. $CaFe_2As_2$

The compound $CaFe_2As_2$ has received much attention in the past year and a half due to the fact that it exhibits many of the properties found in the similar compounds AFe_2As_2 (where A = Ba, Sr), and its parent compound RFeAsO (R = rare earth metal) [1–3]. These compounds exhibit structural and magnetic properties

The $CaFe_2As_2$ sample exhibits similar phases to the parent compounds without the need of doping or oxygen depletion (see Figure 1 for phase diagram) [1]. In fact, the phase transitions can be tuned by applying pressure and magnetic fields. So, in essence it's possible to change the transition properties without changing the stoichiometry of the sample. Again in this sample the superconducting phase only appears after the orthorhombic structural and magnetic transition (which occurs at 170 K under ambient pressure) is suppressed by sufficiently high pressure.

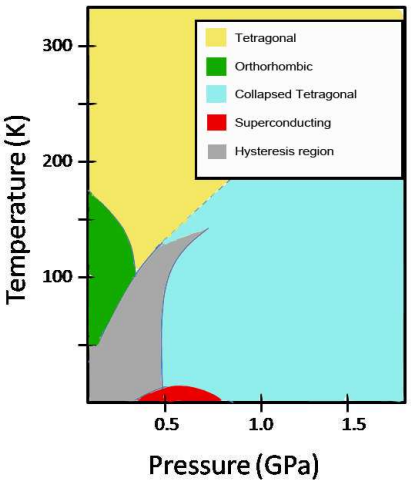

FIG. 1: Phase diagram showing the various phases transitions of $CaFe_2As_2$. [4]

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One of the many advantages in using $CaFe_2As_2$ and some of the its close relatives lies in the crystal structure. The AFe_2As_2 samples are relatively easy to grow as a single crystal [5]. This allows researchers to take advantage of the similarities in the crystal structure to the high T_c cuprates. Both compounds have a two-dimentional electronic structure [5], meaning that most of the electron interaction within the lattice structure takes place within layers of the crystal. $CaFe_2As_2$ has a tetragonal $ThCr_2Si_2$ crystal structure (Figure 2) and can be viewed along the c-axis direction as layers of Ca with Fe-As layers in between [6].

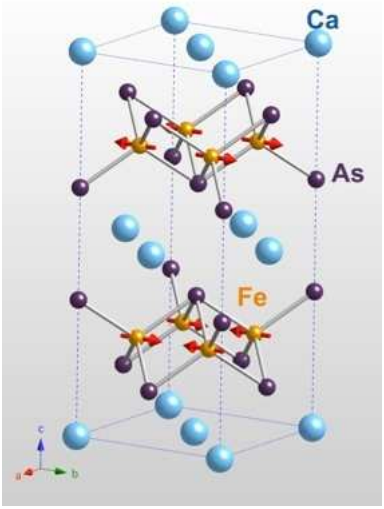

FIG. 2: Crystal structure of $CaFe_2As_2$ [7]

Up to this point, the phases of $CaFe_2As_2$ have been mapped out using only forms of hydrostatic pressure [1, 2, 8]. However, at lower temperatures the media used freezes, at which point the applied pressure may no longer be hydrostatic depending upon the way it freezes. This has caused some discrepancy in the various results provided on the sample [9]. Our goal is to look at a sample using uniaxial pressure, and see if the basic features of the current phase diagrams are preserved, and how they change. In particular we are interested in seeing whether the orthorhombic phase transition suppression still occurs, what the rate of this suppression is, and whether it sill leads to a superconducting phase at low temperatures. If this superconducting phase is still there, we hope to maximize this phase's T_c with pressure tuning.

B. $CeCoIn_5$

$CeCoIn_5$ is one of the members of the the heavy fermion family $CeNIn_5$ (N =Co, Rh, Ir) [10, 11]. These materials all form in the tetragonal $HoCaGa_5$ crystal structure (Figure 3, which is made up of alternating layers of $CeIn_3$ and NIn_2 with the c-axis of the structure perpendicular to the alternating layers [10]. This structure promotes quasi-two-dimensional structural properties very similar to that of the high T_c cuprates [11, 15]. These materials also have fairly low superconducting transitions, which makes it possible to study normal state properties much closer to a quantum critical point, than can be measured in the cuprates [13, 14]. These materials are also easy to grow as single crystal samples and as such are easier to access than similarly structured older materials [10].

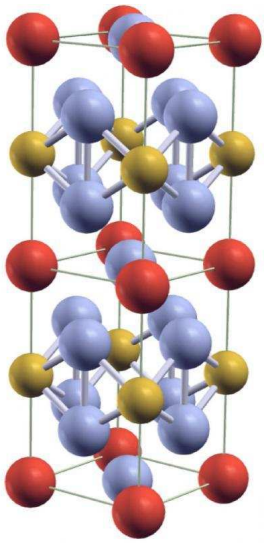

FIG. 3: Layered crystal structure of $CeCoIn_2$ [12]

The material $CeCoIn_5$ has a superconducting transition of 2.3K at ambient pressure [11], but what makes this sample particularly interesting is the way that T_c shifts due to the changing ratio ratio $\frac{c}{a}$, This effect can most likely be attributed to the changing hybridization between the various layers as the pressure changes, but the true mechanisms are still unknown and puzzling for theorists and experimentalists alike [13]. Predictions of how T_c and the ratio $\frac{c}{a}$ are related with uniaxial pressure on both the a-axis and c-axias have been made using low temperature thermal expansion [16], and some experimental work has been done with hydrostatic pressure [13], and by doping [10]. The advantage of uniaxial pressure application is that it has obvious and direct effects the lattice constants.

Measurements on the how the lattice constants changed under a and c-axis uniaxial pressure in the sister compound $CeIrIn_5$ have already been measured with success [17] and results are being analyzed from the measurement of c-axis pressure measurements on $CeCoIn_5$. The problem with measuring a-axis pressure of this sample is that the crystals have a tendency to grow in sheets with the broad face perpendicular to the c-axis. Due to

the nature of uniaxial pressure, the small size of faces perpendicular to the a-axis makes applications of uniaxial pressure difficult. We prepared such a sample, and made the measurements of how T_c changes as pressure is applied to the a-axis.

II. EXPERIMENTAL METHODS

A. equipment

Both samples were mounted on a dilution refrigerator to take data (see Figure 4). The fridge is immersed in liquid He which has a boiling temperature of 4.2 K. Then the fridge can be further cooled to about 1 K by using a 1 K pot. Pumping on liquid He contained in the 1 K pot causes the vapor pressure to decrease so more He evaporates, and the temperature of the system decreases. For the current samples, there was no need to decrease the temperature further than 1 K, but if needed the fridge temperature can be lowered even further by pumping on a ^{3}He-^{4}He mix. To adjust the temperature and make sweeps around the transition temperatures, a small heater mounted next to the 1 K pot was used. For measurement of the structural transition temperature on the $CaFe_2As_2$ sample, much higher temperatures were needed, so the fridge was cooled using a hand dewar of liquid nitrogen.

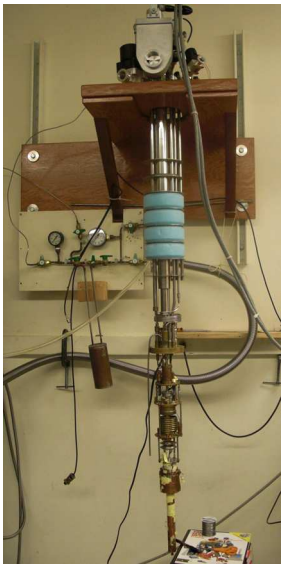

FIG. 4: The dilution refrigerator used in taking data

Uniaxial pressure is applied by using the pressure column at the base of the fridge (see Figure 5). He gas is pumped into the bellows at the top of the column. This pressure in the bellows causes expansion, increasing pressure against the column above the sample, and in turn on the sample itself. This pressure induces a change in voltage difference across a piezo crystal. This voltage difference is then converted into a pressure on the sample using a constant generated by the surface area of the sample in use. Both the measurement and application of the pressure require that the samples be extremely smooth, and that the sides where the pressure is applied are parallel. If they are not, the surface area calculation is inaccurate, meaning the calculation of the applied pressure is incorrect. Also, if the surface is uneven, the pressure will not be applied uniformly to the sample.

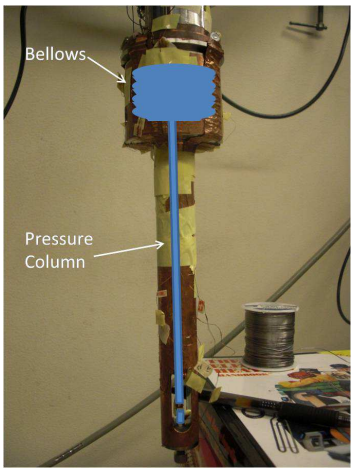

FIG. 5: The pressure column on the bottom of the fridge. He gas is pumped into the bellows, causing them to expand putting pressure on the sample

B. measurements

Two types of measurements are used to detect phase transitions in these samples; resistivity and susceptibility. Resistivity in $CeCoIn_5$ falls off to nearly zero far before the temperature range of interest, so attempting to use the resistivity to detect changes in T_c is futile. Because of this, susceptibility measurements are used for this sample. For the $CaFe_2As_2$ sample, susceptibility measurements are difficult to make because it takes a large magnetic field (upwards of 5 tesla) to see the changes in the susceptibility for the structural transition. So 4-wire resistance measurements are made when investigating this transition, while susceptibility measurements are made while looking for the superconducting transition at He temperatures, where the signal is much better.

Susceptibility measurements were taken using a double susceptibility coil shown in Figure 6. The sample was placed inside one of the two inner secondary coils. An alternating current is passed through the outer primary coils, which induces an EMF through the inner secondary coils. The secondary coils are nearly identical except that they are wrapped in opposite directions. With no sample in the coils, the EMF induced should completely cancel. This way when the sample is placed

inside one of the secondaries, only the change in EMF is recorded. This method greatly reduces the noise in the susceptibility measurements. When a sample goes superconducting, it expels all magnetic field (the well known Meissner effect) and this effect is what is recorded in the susceptibility measurements. Ideally the coils should be just large enough so the sample goes inside, this way the largest effect will be recorded. If there is a lot of extra space in the plane of the sample in the coils, or the sample is not centered in the coil, the change in susceptibility will be much smaller.

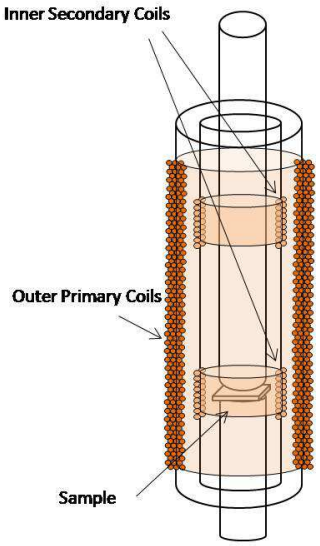

FIG. 6: Double susceptibility coils used in measurements. The use of two secondary coils decreases the amount of noise found in the measurement

Resistance of the $CaFe_2As_2$ sample was measured using a classic 4-wire measurement (shown in Figure 7). In a 4-wire measurement, two wires are attached to each side of the sample. A current is then applied across the sample (one wire on each side of the sample), and the voltage drop across the sample is measured with the other two wires. The resistance can then be calculated directly from Ohm's law: $V = IR$. Using this method of finding the resistance, only the resistance of the sample is measured. The resistance of the sample used was on the order of $100m\Omega$, which is about an order of magnitude smaller than that of the wires used to make the measurements. Since the voltage drop is only measured across the sample and not the wires, this method removes allows the resistance of the sample to be taken while neglecting that of the wires.

Because of the way in which pressure is applied to the sample, it is necessary to attach the leads for the 4-wire measurement to the the sides of the sample. If they were attached to the top or bottom of the sample, the surfaces would no longer be completely smooth,

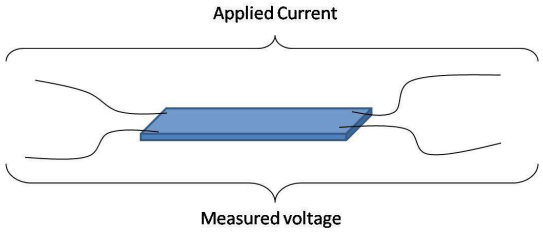

FIG. 7: Classic 4-wire measurement: A current is passed through two wires across the sample, and a voltage difference is measured across the other two. The resistance is found using Ohm's law

causing inaccurate measurement and application of the pressure, as described above. However, due to the extreme thinness of the $CaFe_2As_2$ samples, attaching leads to the edge of the samples is extremely difficult. In an effort to avoid doing this, we decided to make a four wire measurement slightly differently.

The sample is kept in good thermal contact with the fridge by the use of copper strips on the upper and lower pieces of the pressure column touching the sample. Instead of attaching leads to the sample itself for the 4-wire measurements, the leads were attached to the pieces of copper (see Figure 8). While this version of the resistance measurement still neglects the resistance of the wires themselves, it does measure the resistance of the the interface between the copper strips and the sample. With little applied pressure, this resistance is about $30m\Omega$ per interface, so about $60m\Omega$ total, which is about the same order of magnitude as the sample . While it does not cover up the transition, it does slightly suppress the apparent change in resistance.

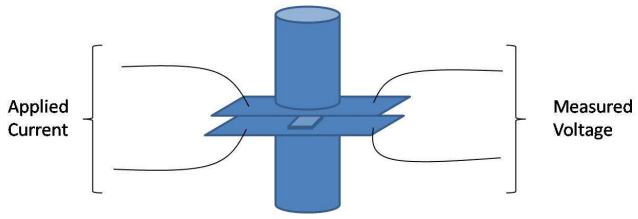

FIG. 8: Our method of using a four wire measurement. Leads are attached to the copper strips which are pressed into contact with the sample by the pressure mechanism.

Another problem with this version of the measurement is that the resistance of the sample itself is smaller than the traditional 4-wire measurement because of the direction of the current. In the adjusted 4-wire measurement, the current is passing through the broad faces of the sample, and since resistance is inversely proportionate to the cross sectional area of the sample, the resistance is smaller than that of the method shown in Figure 7.

C. Sample Preparation

Sample preparation was by far the most time consuming part of working with these two samples. For the $CeCoIn_5$ samples we were interested in measuring the dependence of T_c on uniaxial pressure applied to on the a-axis. However, these crystals grow in sheets with the c-axis perpendicular to the broad sides of the sample. This makes pressure applied on the a-axis very tedious to measure, because the sample is exceptionally unstable when pressure is applied against the skinny ends of the sample.

The first method proposed to account for this challenge was to use varnish to build a multilayered sample oriented in the same direction (see Figure 9). This would allow pressure to be applied onto the a-axis (which would be a broad side of the composite sample). While this method could still be used to make these measurements, we opted not to use this method for several reasons. Primarily, each sample used in the composite sample would need to be x-rayed several times; once to find the correct orientation before polishing the wanted side of the sample, again after the polishing is finished to verify the correct orientation, and possibly more times depending on the amount of polishing used. Second, After the sample was compiled, it would need to be polished as a whole. Our current method of polishing would destroy the varnish holding the pieces together, and the composite would have needed to be assembled again after every face was polished. This allows for a large amount of error in the orientation of each individual sample unless a verification x-ray was taken after each face was polished. While these problems can potentially be solved, we decided this method was impractical given the amount of time available.

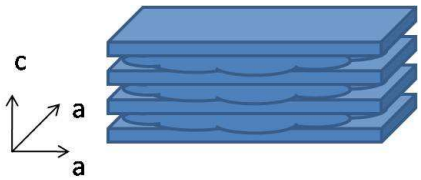

FIG. 9: Proposed method of making a-axis pressure measurements on $CeCoIn_5$ samples

The alternative method we decided to pursue was to search through the many individual samples available for samples that appeared to be slightly thicker than others and polish these down to dimensions that would be more stable if pressure was applied to the sample. This method also had several drawbacks. The thicker samples tended to be multiple samples which had merged together during the growing process, and this didn't always occur perfectly. Often there were small air pockets and other imperfections which needed to be polished out. These polished samples ended up being extremely small (see Figure 10), as much as $\frac{1}{5}$ the size of the samples used in c-axis pressure measurements. This meant that susceptibility signal decreased immensely for these ssamples.

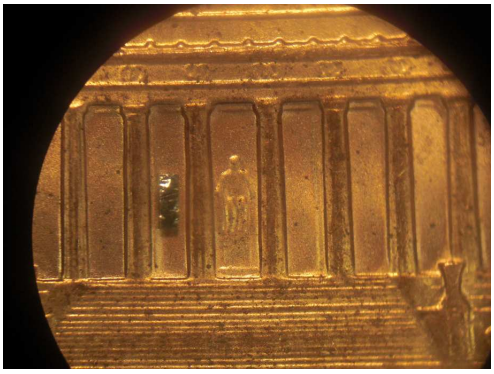

FIG. 10: $CeCoIn_5$ sample placed on the tails side of a penny under of microscope with a magnification of $\times$ 30 for comparison of size. The sample is the small grey rectangle beside the statue of President Lincoln. This particular sample had a mass of .33 mg.

The method used for polishing the samples is straightforward and uncomplicated. The sample is mounted onto a stainless steal spacer using crystal bond. The spacer is then attached to a hand held polisher, where the sample can be raised or lowered to allow the desired thickness of the sample to be polished off. The polishing paper ranged from a 1 micron grit to a 30 micron grit. After the sample is polished to the desired thickness, the crystal bond is dissolved using acetone.

To determine the orientation of the $CeCoIn_5$ samples, Laue x-ray scattering is used. The resulting pattern is compared to the pattern of a theoretical orientation of the crystal in a MATLAB program created by a member of our group.

The $CaFe_2As_2$ samples also proved to be difficult to prepare. In addition to the problems with attaching leads to the sample for a 4-wire resistivity measurement, the samples also proved to be notoriously difficult to polish to a clean surface. Often times during the polishing process the samples develop small cracks along the surface. This could be the result of several different things. It could be a reaction to the acetone or crystal bond. The thermal cycling needed to heat the crystal bond could also be causing these cracks to form. Another problem encountered was that the crystal surface seemed to smear during the polishing. These crystals are grown in a tin flux [8], and there may be pockets or even layers of tin inside the sample that are allowing the crystal to slide a little bit.

In the end, the best way to get a good smooth sample was not to polish them, but to look through

the available samples and find one that was naturally smooth and nicely shaped and cut off any bad edges using a sharpened razor blade. This method could be improved by using another method of cutting the edges of the crystal off (possibly a diamond cutting technique) as it was difficult to use the razor blade to cut the edges in a manner that didn't damage the rest of the crystal.

III. RESULTS

A. $CeCoIn_5$

Due to the small size of our sample compared to the size of the susceptibility coils, our signal was poor and the raw data needed to be averaged to discover any trends in the transitions. To accomplish this a fast fourier transform was used. Data was taken at five different pressures. The absolute pressure on the sample during the different data points is unknown, as the pressure on the sample changes as the fridge is cooled down to He temperatures. Because of this, the points marked P=0 kbar are referring to no added pressure, and all other pressures refer to the pressure relative to this point. The data taken in at various pressures is shown in Figure 11.

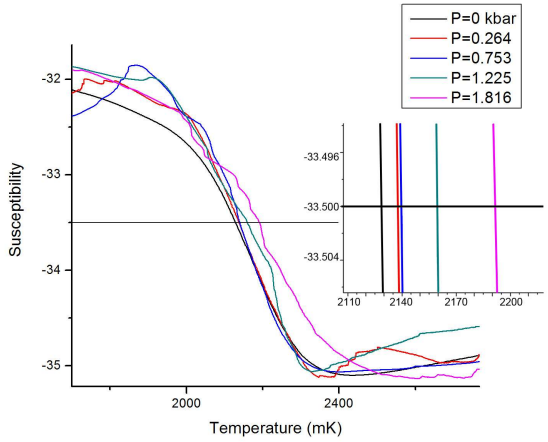

FIG. 11: Transition data at five different pressures. The T_c is taken to occur in the middle of the transition, which in this data has been normalized to occur at a susceptibility of $33.5\mu\Omega$. The inset shows a closeup of of this transition to show the temperature where this occurs.

T_c was taken as the temperature at the center of transition (midway between the maximum and minimum susceptibility measurement). As the pressure is changed the susceptibility measurement changes by some constant offset. This was corrected for in each run and normalized to a transition at a susceptibility of $33.5\mu\Omega$. In Figure 12 the transition temperatures have been graphed vs. the relative pressure of the run, along with a line of best fit. The error bars on the various points represent the error caused in the changing susceptibility baseline between the various runs and correcting for this. Our data shows a relative increase in T_c of about 60 mK in a pressure increase of about 2 kbar.

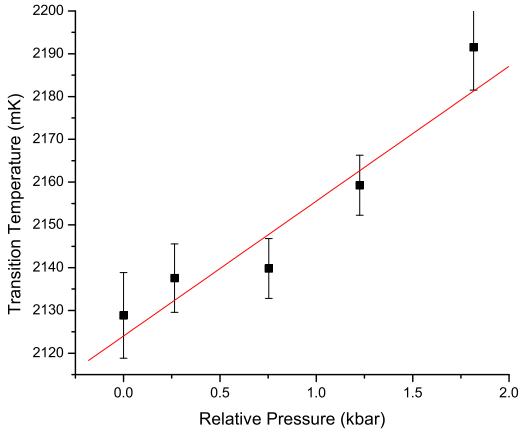

FIG. 12: Pressure vs. transition temperature for the various runs graphed along with a best fit line. See text for further information.

B. $CaFe_2As_2$

Our method for looking at the structural transition with resistivity through the copper contacts yielded exceptionally poor results. The transition was not obvious at all, and in many runs there appeared to be several possible points for the transition. To further complicate matters, the transition is first order and therefore has a hysteresis which makes this transition more difficult to follow.

Susceptibility results seem to indicate a superconducting dome in this sample, however the exact nature of how the dome depends on magnetic field and pressure has not been determined. These measurements were taken on a cool down after my time in the REU program and have not been fully analyzed at this time.

IV. CONCLUSION

While the data for the $CeCoIn_5$ sample looks convincing there were several issues with it. First of all, because of the size of the sample compared to the susceptibility

coils, the data had lots of noise in it, making the transitions hard to nail down even after the averaging on the results was completed (see Figure 13). These transitions were further complicated by the change in susceptibility we experienced at different pressures. Small shifts in the overall susceptibility can have an effect on where the T_c of the run occurred in relation to the other runs. Another problem with our sample was that at the end of the run, the sample was obliterated. This raises concerns about when this occurred (beginning, middle, or end of the run), and how much this effected our results.

Considering the various problems we experienced, the general trend observed is most likely still accurate: as pressure is experienced on the a-axis of the sample, the T_c increases. In fact, our results of an increase in T_c of 60 mK for a 2 kbar pressure increase match up very well with those predicted by thermal expansion [16]. Unfortunately, confirmation of our results is needed before any certain conclusions can be drawn.

Efforts have already been made to create a susceptibility coil whose size more closely matches that of the samples, and the signal is improved imensily (see Figure 13). It would also be helpful if a larger sample could be prepared for a-axis pressure measurements.

When the true relationship between T_c and the pressure can be determined, it would be exceptionally interesting to determine the various lattice constants at various pressures and see how the ratio $\frac{c}{a}$ changes the pressure. Also this data should be compared to that of uniaxial pressure on the same sample. If a general trend can be found, comparison to similar tests on similar samples such as $CeIrIn_5$ could provide more general trends in this family of materials.

Much more work still remains for the $CaFe_2As_2$ samples as well. First the data generated from the last cool down needs to be analyzed more thoroughly to discover properties of the superconducting dome. Additionally, the temperature region of this transition makes it tricky for making measurements, and the method for doing this needs to be improved.

It is still necessary to discover what is happening with the orthorhombic structural transition around 170 K under pressure, and to see whether the suppression of this phase is leading to the superconducting dome. To this end a method of measuring the resistance of the sample while uniaxial pressure is applied needs to be found which minimizes the resistance of everything except for the sample.

While a lot of work was done on both $CaFe_2As_2$, and $CeCoIn_5$ this summer in both sample preparation and actual measurement, a lot of work still remains. If sample preparation can be improved for these samples, the data can be taken much more easily and quickly. However, both samples appear to be exhibiting the transitions which we're interested in, and have so far generated very promising results.

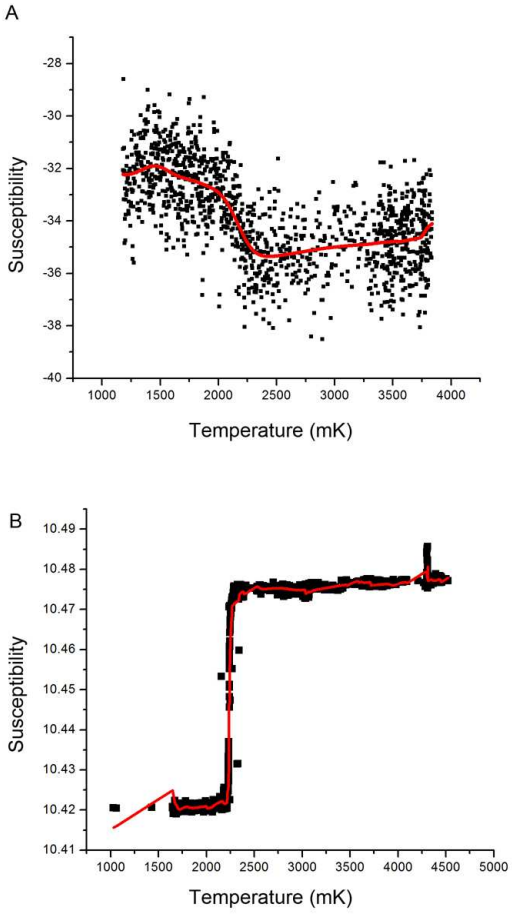

FIG. 13: Figure A shows one of the susceptibility runs from the data analyzed in this paper, along with the averaged line in red. The data is very noisy with a spread of about $4\mu\Omega$, compared with a the transitions jump of about $3\mu\Omega$. The transition is also very broad (About 300 mK). Figure B shows data from a new susceptibility coil whose size is much more comparable to that of the sample. Here the data is much less noisy with a spread of about $0.005\mu\Omega$ compared with the transitions jump of $0.055\mu\Omega$ a much high signal to noise ratio. In addition the transition seems to range only over about 10-20 mK.

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