

Low temperature experimental techniques for detecting structural and magnetic transitions in $(\text{CH}_3)_2\text{NH}_2\text{CuCl}_3$

Sara Gamble
Department of Physics, University of Florida
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Abstract

The discovery of several high critical temperature superconductors in the cuprate family has produced an elevated interest in low-dimensional systems (two dimensional planes or one dimensional chains) that retain the basic characteristics of these cuprate crystals in a simplified form. As a result of this link, an understanding of the structure and behavior of low-dimensional systems has become key in understanding the phenomenon of high temperature superconductivity. In order to study one such system, $(\text{CH}_3)_2\text{NH}_2\text{CuCl}_3$, also known as MCCL, for structural and magnetic phase transitions, samples of protonated and deuterated versions of the material in powder form are used as a dielectric in a copper parallel-plate capacitor, as a transition in the MCCL will produce a detectable change in the dielectric constant of the sample. The capacitor is housed in a sample cell and bolted to the base of a cryogenic probe capable of reaching 4.2 K. As the sample is cooled and warmed, a lock-in amplifier sends an excitation voltage to a capacitance bridge wired to the cell and the bridge is subsequently balanced to null the reading from the sample. Any change in capacitance disturbs the balance of the bridge and these deviations from null are monitored on separate X and Y channels, the magnitude and the phase of which are then graphed as functions of temperature to look for the transitions. The results suggest a structural transition in MCCL at 239.7 K, associated with the freezing of rotational degrees of freedom in the $(\text{CH}_3)_2\text{NH}_2$ groups, and a magnetic transition at 16.6 K, which is conjectured to be associated with antiferromagnetic alignment.

I. Introduction

Every material capable of undergoing a superconducting transition has a different critical temperature (T_C) at which its resistivity (ρ) goes to zero and, correspondingly, its conductivity ($\sigma = 1/\rho$) goes to infinity. One common characteristic of these temperatures is that they are all relatively low, usually falling below 10 K for type I superconductors. Thus, it was unexpected to discover a copper-oxide material with $T_C = 30$ K in 1986 and dozens more “high T_C ” cuprates

with critical temperatures as high as 133 K in the subsequent years. Theory still does not offer a satisfactory explanation as to why these materials possess this characteristic [1].

One feature common to many of the high T_C cuprates is the presence of copper-oxide (CuO_2) planes in the crystal structure that are weakly bound by ions that form the charge reservoir for the superconductor. In the full crystal, however, the distance between the ions that form the planes is significantly smaller than the distance between the planes themselves and, as a result, electrons are more likely to remain confined to the two dimensional (2D) surface than to move to an adjacent plane. This limitation to what can be approximated as 2D movement enables one to model the complex three dimensional (3D) structure of the cuprate as a physically and mathematically simpler plane [2].

After the reduction of the 3D crystal problem to a 2D planar one, a further simplification still exists. In some cases, within each of these planes of copper spins the ions are bound to one another in ladder structures in which single one dimensional (1D) chains of ions bond together and subsequently undergo interchain coupling. In this coupling, ions form bonds between two of the 1D chains of comparable strength to the original bonds that hold the backbone of the chain together [3]. Thus, the strength of the copper spin interaction, J , between the “sides” and the “rungs” of the ladder are roughly equal. Because mathematical calculations for the diagonalization of the Hamiltonians of these systems with reasonable J values are still quite complex [2], it is desirable to study even further simplified 1D crystal structures composed of alternating chain materials. In these materials, the J interaction parameters are no longer equal and in fact alternate between two different values [4]. As a result of these differing J values, the magnetic spins are arranged in a roughly linear geometry and the two dimensionality of the ladder is lost in favor of a 1D zigzag chain. It is this structural simplicity of the 1D alternating

chain type crystals that has made them an excellent candidate for the study of the high temperature superconductors, as they possess the basic structural characteristics of the 3D stacking cuprate planes without the physical or mathematical complexities.

The purpose of the experiment described herein is to utilize a low temperature cryostat to study the structural and magnetic phase transitions of one of these 1D alternating chains. In order to detect changes in the crystal structure, we use our sample powder as a dielectric in a copper parallel-plate capacitor placed in the cryostat. As the sample is cooled to and warmed from 4.2 K, we watch for a change in the dielectric constant of the powder as a function of temperature as an indicator a transition has taken place. The change in the dielectric constant is detected via a change in the capacitance of the system and this alteration is, in turn, measured with a balanced capacitance bridge and lock-in amplifier. The data are recorded with the aid of a LabView program.

II. Methods

A. Sample Structure and Experimental Cell

The chain selected for this experiment is catena(dimethylammonium-bis(μ_2 -chloro)chlorocuprate), $(\text{CH}_3)_2\text{NH}_2\text{CuCl}_3$, also known as MCCL. R.Willett used X-ray diffraction to determine the crystal structure of MCCL at 300 K (see Fig. 1) in which one can see the chain of $S=1/2$ Cu^{2+} spins with bonds of 3.411 Å and 3.547 Å between every other Cu atom. It is this distance difference that gives rise to the two distinct J values. Further, neutron scattering, electron paramagnetic resonance (EPR), and magnetic susceptibility experiments indicate that MCCL undergoes a structural transition at approximately 250 K where there is thought to be a locking of the rotational modes of the $(\text{CH}_3)_2\text{NH}_2$ groups seen on the edge of the structure.

There is also thought to be a magnetic transition in MCCL, somewhere between 10 K and 50 K, attributed to the antiferromagnetic alignment of the Cu spins [4]. The specific temperature of this second transition, however, has not been determined by the neutron scattering, EPR, or susceptibility measurements, and consequently further study aimed at finding this point requires the implementation of a different experimental technique. It is this need for an alternative that has prompted us to use MCCL as a dielectric in a capacitor, as changes in the dielectric constant of a material are both a signal that a transition has taken place and a quantity in which one can fairly easily monitor fluctuations.

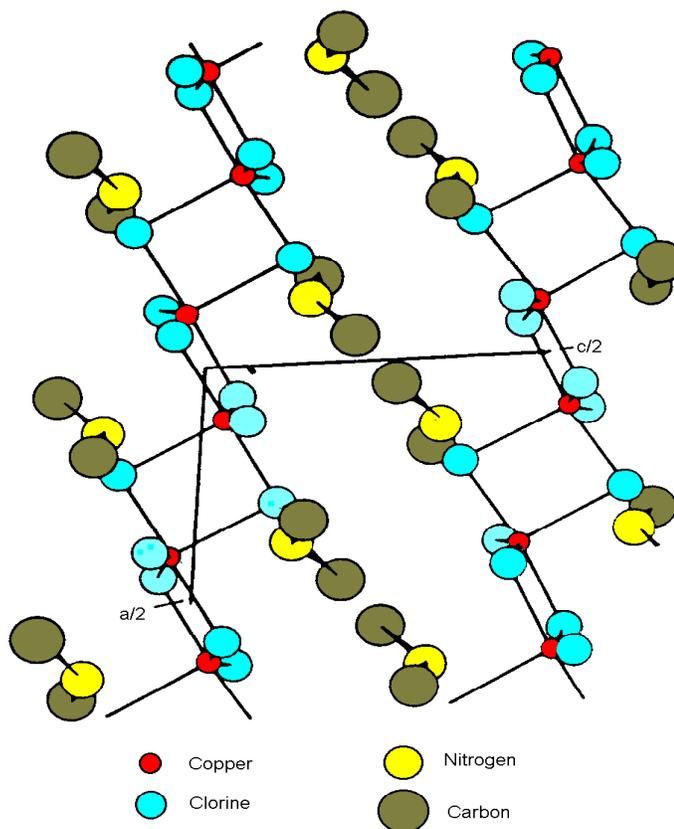


FIGURE 1: Crystal Structure of MCCL. Special note is given to the differing distances between every other copper spin composing the alternating chain structure. All hydrogen atoms have been removed to elucidate the basic crystal structure.

For this experiment we have two samples of MCCL. The first is a protonated powder, and the second is a deuterated version of the same powder. Both samples were synthesized by the Talham group in the UF Chemistry department and have been sitting in desiccators for approximately one year. For each run of the experiment, we placed nominally 7 mg of the sample powder inside a pre-constructed sample-housing cell for the copper parallel plates.

B. Experimental Configuration

Our setup contains three primary components: the lock-in amplifier, capacitance bridge, and sample cell housed inside the cryostat. We expect the capacitance change to produce signal deviations in the microvolt to nanovolt range, and thus our detection mechanism must be extremely sensitive. As a result, we configure and tune each component of our apparatus for both maximum signal acquisition and maximum noise reduction.

The lock-in amplifier actually serves two purposes: first, it supplies the driving AC excitation voltage for the circuit, and second, it provides a means for measuring the change in this voltage due to a passage through the dielectric medium with minimum noise. The lock-in works by generating a constant voltage sine wave by means of an internal oscillator. This signal is then sent out through a generator channel (and in our case through the capacitance bridge and then through the sample cell). After the signal has been sent through the circuit, it returns to the lock-in through a preamplifier for demodulation.

The key to the lock-in's operation lies in its phase sensitive detection (PSD). After the signal is returned through the preamp, the lock-in compares it to the reference signal and, subsequently, gives an output in the form of a DC voltage both proportional to the signal being

measured and as a function of the relative phase angle between the returned and the reference signals. For instance, say the input signal is given by [5]

$$V_i = V_o \sin(\omega + \Delta\omega)t \quad (1)$$

where the angular frequencies of the reference and the input differ by the amount $\Delta\omega$. Thus, there will be a slow varying phase shift

$$\psi = \Delta\omega t \quad (2)$$

which will yield an output, V_b ,

$$V_b = (2/\pi) V_o \cos(\Delta\omega t) \quad (3)$$

where the $2/\pi$ comes from an RC filtering process that has a time constant larger than the period of the reference signal. One specific attribute of the lock-in we utilize in this experiment is that it has two channels, so we are able to constantly measure both a real (lossy or resistive) term on the X channel (RI) and imaginary (capacitive) term on the Y channel ($I/\omega C$). The relationship between the components is established through the phase angle ($\phi = \tan^{-1}(Y/X)$). Through this process of demodulation and decomposition, the lock-in also greatly increases the signal to noise ratio of the measurement. The instrument will, in fact, only detect signals at frequencies very close to the reference frequency and will, through a bandpass filter, eliminate any higher or lower noise. The PSD also works to eliminate noise or interference that might by chance oscillate at the reference frequency, as it will filter any signal not nearly in phase [5]. For our experimental runs, we found an optimum setting for the internal oscillator at 5 kHz and 10 mV. The sensitivity of the measurement was 5 μV and the readings were taken with a time constant of either $\tau = 1$ or 2 sec depending upon what interval of averaging provided optimal signal resolution with stability at any given point during the run.

While the lock-in amplifier can measure any verity of input signals to within a tolerance determined by the settings, there is an optimal way to configure it as to make the obtained measurements more precise. It is perhaps one of the soundest principles of scientific measurement to take all small readings as deviants from a null. Accordingly, since our anticipated change in voltage due to the transitions in the MCCL is on the micro to nanovolt scale, we would like to null out the measurements on both the X and Y channels to look at the anticipated capacitance change from an initial zero reading. For our purposes, the reading about null is accomplished with the aid of a capacitance bridge. A capacitance bridge uses a form of a basic ratio bridge, and the one utilized here employs one calibrated variable standard capacitor and a ratio arm of transformer windings to null the voltage difference between the arm and the known and unknown capacitance. This null voltage across a meter detector in the bridge is that detected by the lock-in. When coupling this bridge with the amplifier in the lock-in, the signal magnitude can increase by as much as a factor of 10^9 . When the phase transition occurs, the capacitive component to our signal changes, and this change unbalances the bridge, which, in turn, causes the lock-in signal to deviate away from null, making it possible to see the transition in both the X and Y channels.

While the use of the lock-in and capacitance bridge greatly reduce the uncertainty in the measurements, further steps are still taken to reduce noise. First, we wire the sample cell inside the probe to the external capacitance bridge via a grounded three terminal scheme utilizing BNC coaxial cables. We do this so that the lines to the sample carrying the current remain near perfectly floating and minimal residual capacitances and noise couple to the signal. Thus, the terminal capacitances of our wiring scheme become inconsequential, and the capacitance measured by the bridge is determined only by the internal geometry of our sample. We also

reduce the noise in our equipment connections (BNC and GPIB cables) by utilizing HP-IB fiber optic connections to hook our electronics into the computer running the LabView data acquisition program.

C. Low Temperature Techniques

The cryogenic probe used to cool the MCCL sample was prefabricated upon the commencement of this experiment and designed to function between 1.5 and 300 K. Because of the range of the estimated transition temperatures of the sample, we only take the sample through the 4.2 K to 300 K range (liquid helium without evaporative cooling to room temperature). In order to do this, we utilize several different low temperature techniques.

First, the probe and its components must be suited to withstand large thermal gradients and yet still be sensitive enough to allow us to detect the voltage output change. To manage this, both the sample cell and the inner vacuum can of the probe were constructed out of copper to reduce error associated with different thermal contractions of the components. In further effort to combat uncertainties associated with thermal differentials, all the wires that ran from room temperature 300 K to the liquid helium 4.2 K environment were thermally grounded. Also, the design of the sample cell allowed for housing in an inner vacuum can inside the cryostat bath that maintains a high vacuum during the entire course of the experiment with pressures never rising above 80 mtorr at room temperature. This can also allows us to introduce small amounts of helium exchange gas into the system to bring the sample cell into thermal equilibrium with the rest of the probe base in an expedient manner and at the same time ensure that the system remains free of impurities that could freeze and damage the electronics at low temperatures. The pressure inside the can with this exchange gas is kept below 1000 mtorr at room temperature.

The can is isolated from the liquid helium/nitrogen bath environment by an indium ring seal that prevents either of these liquids or nitrogen gas from flowing into the vacuum.

Since such a wide temperature range is desirable for our measurements, we rely on resistors for both our thermometry and our heating. The thermometer was factory-calibrated for use with temperatures ranging from 1.5 K to 300 K. An AVS resistance bridge reads the thermometer's resistance value every 22 seconds during the conduction of the experiment, and we greatly reduce the error associated with this read value by implementing a four-wire measurement instead of a conventional two. By having two wires carry the current to the resistor and another two read the voltage drop across it, the lead resistances of the primary current carrying wires can be neglected and thus the bridge reads a most accurate resistance value. The heater used to warm the sample from 4.2 to 300 K is a 100 Ω resistor capable of dissipating 1 W of power. For our sample, supplying 1.742 V to the heater is optimal for warming at the rate of approximately 0.5 K per minute, which is the rate that gives us data points both at an interval small enough to see various parts of the transition, and at a reasonable warming pace.

III. Results

Upon warming the sample of protonated MCCL, we clearly detected the structural transition associated with the freezing of the rotational modes of the $(\text{CH}_3)_2\text{NH}_2$ groups. The lock-in detected a change in capacitance of the sample beginning at 237.1 K, peaking at 239.7 K, and ceasing at 243.6 K. The voltage drop reached a maximum deviation of approximately 5.65 μV from an average equilibrium line between the initial and final magnitude values (see Fig. 2).

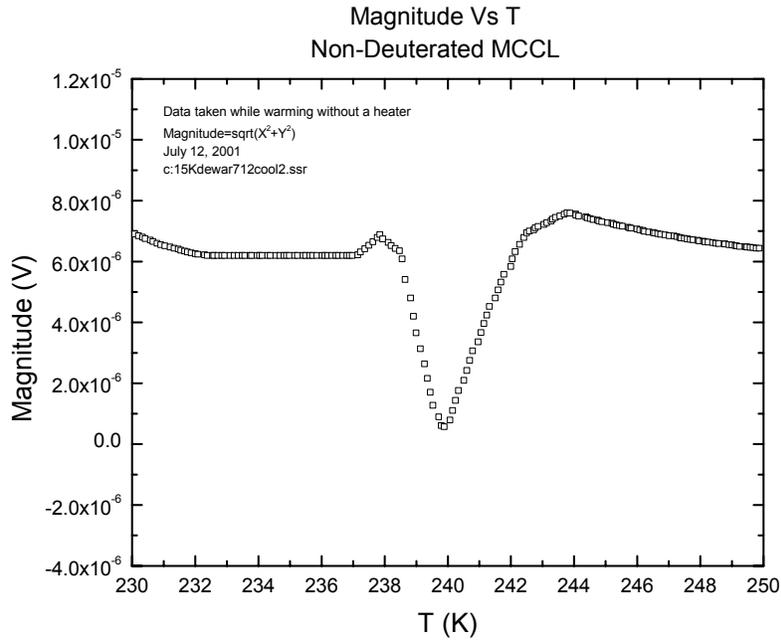


FIGURE 2: Magnitude data for protonated MCCL, indicating a structural transition at 239.7 K. Data taken above 250 K indicates that the capacitance equilibrates at a value approximately .63 nV greater than that prior to the transition

The magnitude of the signal is calculated (magnitude = $\sqrt{X^2 + Y^2}$) and graphed, as opposed to graphing each X and Y channel voltage individually, in order to make any change in the signal from either distinct channel more visible in the plot. Studies of the graphs of the separate channels indicate that at different points in the temperature cycle one channel will usually dominate. When there is a shift in the signal, both channels are affected, but the change is typically only visible in the dominating signal and is, in the other, masked by noise. By taking the magnitude of the combined signal, these small deviations in the subordinate channel become more visible and, consequently, the signal to noise ratio improves.

Associated with this change in magnitude exists a corresponding change in the calculated phase angle. This is manifested as a discontinuity in the $\tan^{-1}(Y/X)$ graph from 239.8 K to

240.0 K. This interval coincides with the peak in the voltage magnitude graph to within 0.2 K (see Fig. 3).

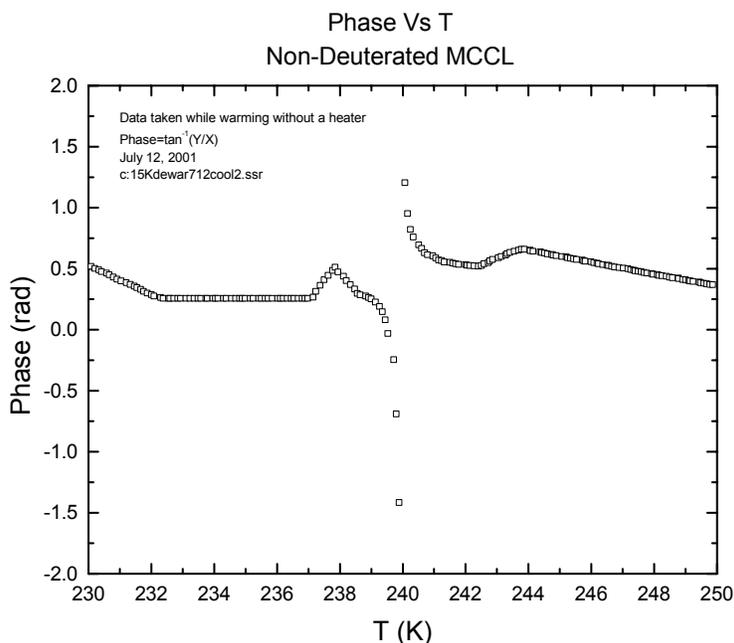


FIGURE 3: Phase data for protonated MCCL indicating a structural transition ~ 239.9 K

After detecting the transition warming the sample from 77 K to 294 K, we subsequently cooled again to check for reproducibility of the data. Three further cool and warm cycles, however, failed to detect the transition and we consequently decided to proceed to the deuterated MCCL. This, perhaps seemingly premature, shift in experimental focus was made in order to attempt to ascertain if the first detection in the protonated powder was a coincidence due to the construction and possible thermal contraction of the sample cell, or if the material is only capable of undergoing the transition with an appreciable magnitude once.

Upon study of the deuterated sample, we first found clear evidence that the MCCL undergoes a transition in the low-temperature region left uninvestigated in the protonated

sample. Through the first cooling there is a pronounced 79.8 nV drop in magnitude which beings at 16.29 K and equilibrates at 16.98 K. The transition held a signal to noise ratio of approximately 4.7. The corresponding phase shift is also seen in the interval 16.34 K to 16.93 K (see Figs. 4 and 5)

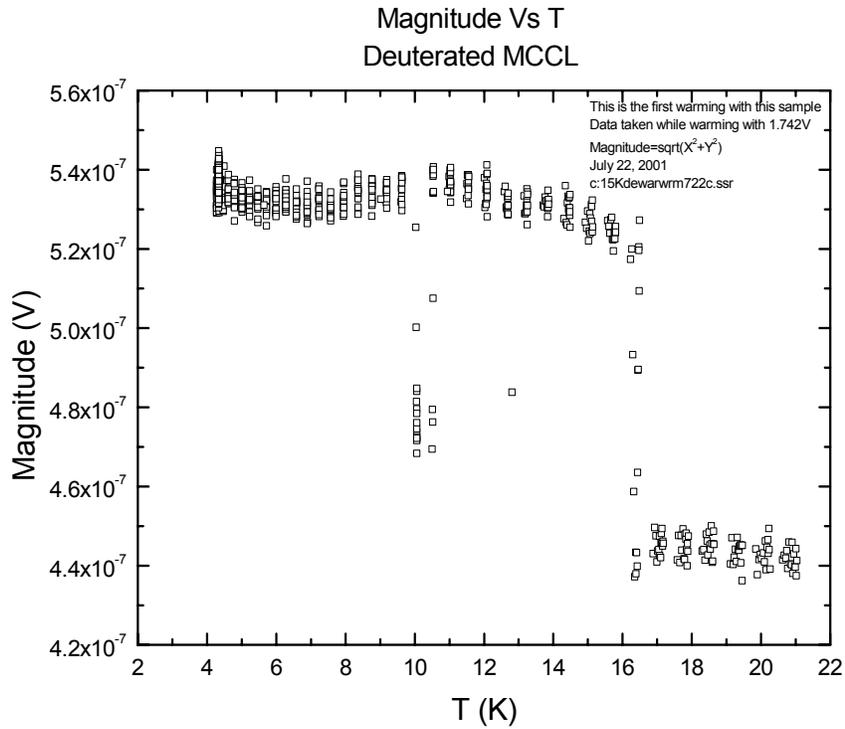


FIGURE 4: Magnitude data for the first warming of deuterated MCCL indicating the existence of an antiferromagnetic alignment transition at ~16.6 K. The drop in magnitude at 10 K is thought to be caused by a variety of thermal noise effects associated with the sample.

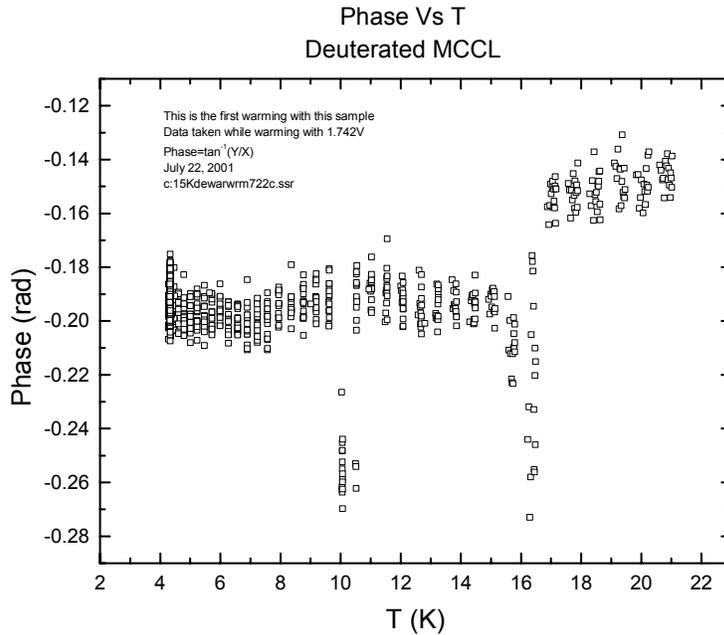


FIGURE 5: Phase data for the first warming of deuterated MCCL indicating a magnetic alignment transition at ~16.6 K. The 10 K dip in voltage is again attributed to the thermal noise.

Upon a second traversal of the suspected transition region, shifts in the phase and magnitude graphs are again seen, but the resolution inherent in the first data set is no longer present and a substantial amount of noise becomes evident. While the magnitude data suggest the commencement of a ~342 nV transition at 16.03 K, the voltage signal does not reach a stable equilibrium until 39.48 K. The signal to noise ratio correspondingly decreases to 2.8 (see Fig. 6). Similarly, the phase data indicate a shift beginning at 16.00 K and sample equilibration at approximately 33.36 K (see Fig. 7).

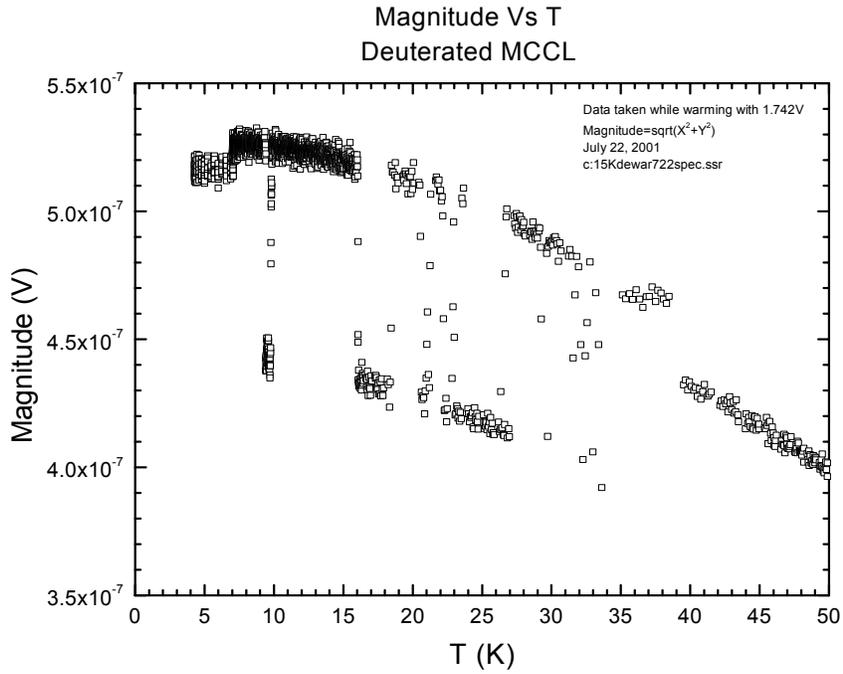


FIGURE 6: Magnitude data for the second warming of deuterated MCCL from 4.2 K to 50 K. Analysis of this graph elucidates the association of the drop in voltage at 10 K with noise coupled to the sample.

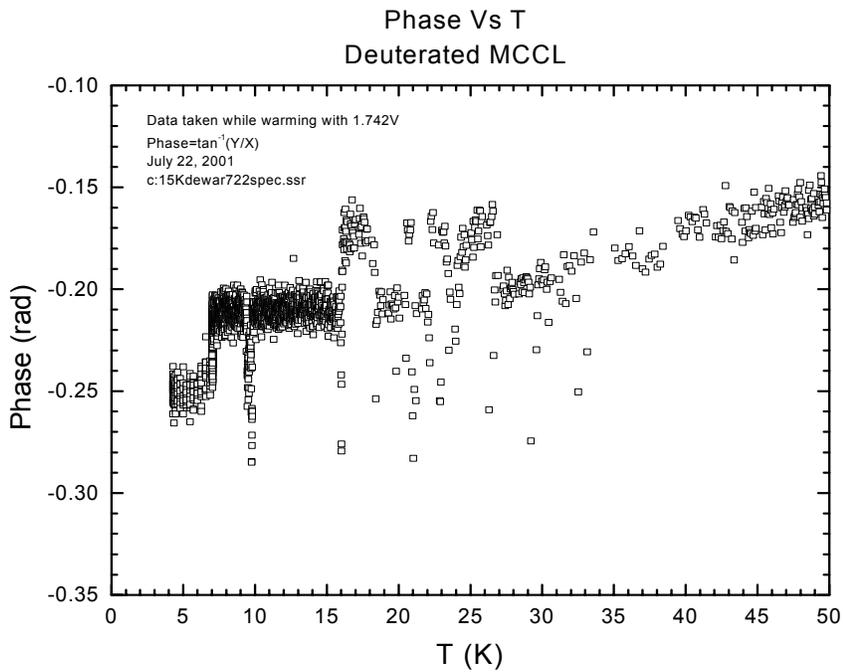


FIGURE 7: Phase data for second warming of deuterated MCCL from 4.2 K to 50 K

A similar loss of signal resolution occurs as the second warming of the deuterated MCCL traverses the suspected 240 K transition range. While a transition is seen, the range is not as defined, spanning from 227.20 K to 233.01 K (see Figs. 8 and 9).

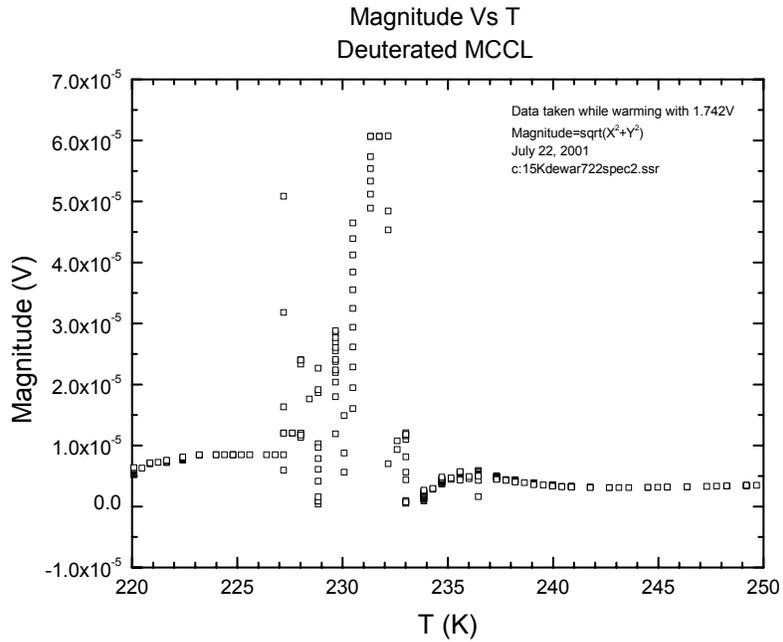


FIGURE 8: Magnitude data for the second warming of deuterated MCCL from 220 K to 250 K

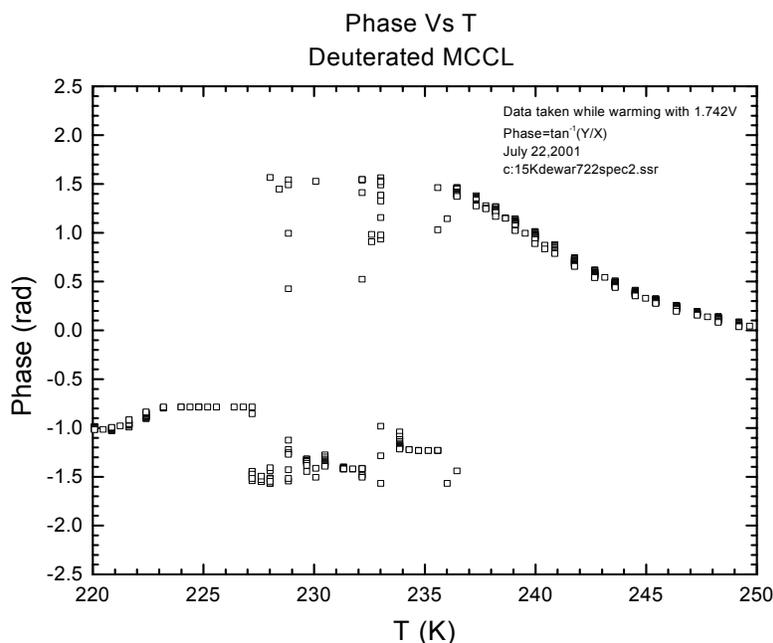


FIGURE 9: Phase data for second warming of deuterated MCCL from 220 K to 250 K

IV. Discussion

The data collected reaffirm the existence of the suspected structural transition at 239.7 K and further strongly suggest the existence of a magnetic transition at 16.6 K. The structural transition is still thought to be associated with the freezing of the rotational modes of the $(\text{CH}_3)_2\text{NH}_2$ groups as previously indicated by the neutron scattering experiments. The previously unseen magnetic transition at 16 K is thought to have its source in the antiferromagnetic alignment of the alternating Cu spins in the chain structure. This magnetic alignment scheme would make sense, as the bonds between the spins are approximately 90° , a bond angle typically associated with such antiferromagnetism. There are, however, several factors that one must consider before putting these conclusions in perspective.

First, one must consider the integrity of the MCCL samples. In its pure form, MCCL is an insulator and, correspondingly, well suited as a dielectric. The samples we used here, however, were synthesized over one year ago and over the course of time have slightly oxidized. This oxidation altered the electrical properties of the samples actually making them conducting at room temperature. After one run of the protonated MCCL, the sample conducted in the temperature range from 300 K to 77 K, and it was this conductivity along with the non-reproducible nature of the 239.7 transition that prompted us to move on to the deuterated material. The deuterated MCCL also conducted at 300 K, but upon pumping a high vacuum on the sample (6 hours to 60 mtorr) enough impurities were removed to obtain a room temperature capacitance measurement. The existence of transitions in the regions where the previously conducted neutron scattering predicts them lends credence to the data, yet it is currently undetermined if this oxidation has a strong effect on the crystal structure of MCCL.

The loss of the defined nature of the transition and the coupled decrease in the signal to noise ratio upon each warming could be indicative of several different phenomena. First, the crystal structure of the MCCL may lose some of its structural integrity upon each cooling to low temperature. The lattice may simply break down as heat is removed and after warming is not able to reform itself in its original, clearly defined, alternating chain organization. Second, the possibility exists that after the first cooling and subsequent warming not all of the rotating $(\text{CH}_3)_2\text{NH}_2$ lock, or correspondingly unlock, each time the transition region is crossed. Some will remain in the same state and the change in the signal will correspondingly lessen and lose clarity simply due to the number of spins undergoing the transition. Finally, the increased noise

and apparent difficulty that the sample experiences in re-equilibrating could be the result of a poor experimental design. In order to tightly pack the MCCL in the sample cell, we placed a spring between the actual cell housing and the top plate of the copper parallel-plate capacitor. Thus, it is possible that the crystal structure did try to reform after the cooling but simply could not construct the large lattices it was previously composed of as a result of the large spring force compressing it.

While the existence of the transitions is clear as a phenomenological occurrence, one must also consider the possible thermal lagging of the actual sample powder to that of the thermometer used to read the temperature inside the cryostat. In the probe construction, the thermometer is mounted closer to the 100 Ω heater than is the sample, and the sample is also housed inside a large copper cell that acts as a partial heat sink. Thus, there exists the possibility that the thermometer reads temperatures that are lower than the sample while cooling and higher while warming. In order to minimize this thermal lagging, minimal amounts of liquid nitrogen and liquid helium are introduced to cool the sample at the slowest possible rate, the DC power supply delivers the minimum voltage necessary to warm the sample in a timely fashion, and the LabView code is written in order to take data points in intervals that give the sample time to come into thermal equilibrium with the surroundings. Also in the area of temperature control, it is a limitation of our current equipment configuration to directly control the temperature of the sample. Hand calculations were performed to correlate voltage values sent by the DC power supply to corresponding temperature differentials in the sample in different temperature ranges, as the voltage is the controllable variable. In future runs, we would like to utilize a proportional/ differential/ integrator temperature controller that will

enable us to input a set point in the form of a desired temperature and subsequently have the controller adjust the heater to bring the sample to that set point.

V. Conclusions

The examination of structural and magnetic phase transitions of MCCL by way of using protonated and deuterated powder versions of the sample as a dielectric in copper parallel plate capacitor indicates a structural transition at 239.7 K and a magnetic transition at 16.6 K. The 239.7 K transition falls in line with the expected temperature value predicted by previously conducted neutron scattering experiments and corresponds with the freezing of the rotational degree of freedom in the $(\text{CH}_3)_2\text{NH}_2$ groups on the edge of the alternating chain structure. The formerly unseen 16 K transition falls within the 10-50 K transition window earlier hypothesized and corresponds with the antiferromagnetic alignment of the Cu spins. The acquisition of this data has lent credence to our experimental set up of utilizing the MCCL as a dielectric and detecting changes in capacitance via cryogenic cooling, bridge balancing methods, and lock-in detection. Thus, the technique has demonstrated its applicability to other low-dimensional systems that model the structural characteristics of high critical temperature cuprates.

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