Ecole Polytechnique Fédérale de Lausanne

AC-measurements of specific heat in BCPO

TP4 project report

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Contents:

1. Introduction:

This report is a summary of my TPIV project for the first master semester, which has been done in laboratory of quantum magnetism, LQM, at EPFL under the supervision of Pr. H.Ronnow and the post-doc J.Antonio Larrea Jimenez. The main goal of this project is to investigate the effect of the Zn impurity (in small amount, 0.01) in the specific heat of BiCu2PO$_6$ in low dimension.

This project has 2 parts; its first part which was the Cp measurement for zero pressure, was completed in this semester, and the second part which refers to the same measurement by applying high pressure, will be done in the second semester.

Recently many investigations around the spin-gap (SG) anti-ferromagnetic systems (AFM), especially in low dimension, have been done. For example, BCPO is one of the interesting SG groups that some of its properties such as magnetic susceptibility or specific heat under different conditions, such as low or high temperature or pressure, have been investigated. For instant, studying the change in its magnetic susceptibility and specific heat behavior because of being doped by different kinds of impurities such as Zn, Ni or Ca, due to the change in its structure, is one of the verified cases. The idea of comparing the Cp of BiCuPo6, doped and un-doped, in low pressure and high pressure, by the use of AC calorimetry, is an interesting case which for the first time was done in this project, and fortunately the result of this experiment had a good matching with presented theories.

2. Sample:

Two samples in this experiment are from the BCPO group; the first one is BiCu2PO6 without any additional impurity, and the second one is $Bi(Cu0.99Zn0.01)_2PO_6$ which is doped by Zn; a non-magnetic element. In this doped material, the Zn^{+2} have been introduced on the Cu^{+2} site. Both of them are anti-ferromagnetic and single crystal.

2.1. Crystal structure:

The BCPO has a spin ladder structure which can be assumed as a structure between 1-D; Heisenberg system without any Long Range Order (LRO), and 2-D system, in which quantum fluctuation is considerable. The unit cell contains 2 different Cu (Cu1 and Cu2), which create Cu sites, and 4 different O (O1-O4) which create O sites. The structure composed of 2 deformed square pyramids of CuO5, in each pyramid the Cu^{2+} is at the center of 5 Oxygen. These two square pyramids have two different kinds of CU, which create a dimer (with the distance 2.8A), and one shared edge of a pair of basal OxygenO2. Each dimer, along the b axis, connects to two others via its four O1, in a zigzag double chain and create ladder. Bi is located between two ladders in a b-c planes which are separated by PO4 tetrahedral. This tetrahedral connects two consecutive dimmers by their O2 and strengthens their connection (figure1). The Cu-O-Cu angle in the leg is 112 and along the rung is about 92 degree. [2]

$BiCu_2PO_6$ is a zigzag two-leg spin ladder; which is one of the well-known of Spin-Gap systems, because of its even numbers of legs. Its spin gap is equal to $\Delta/k_\beta = 34K$. This spin gap can be determined by susceptibility and heat capacity measurement.

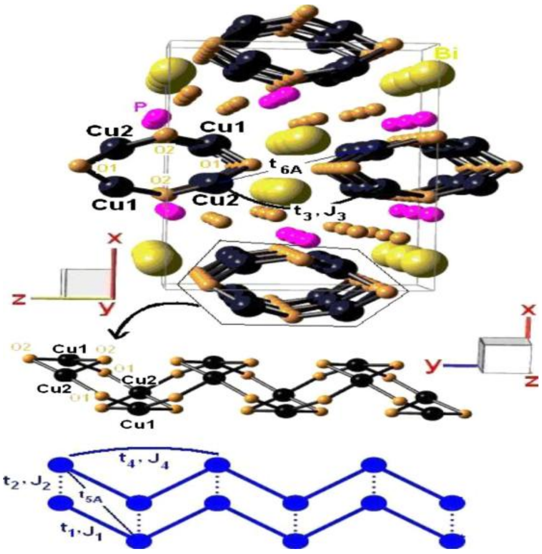
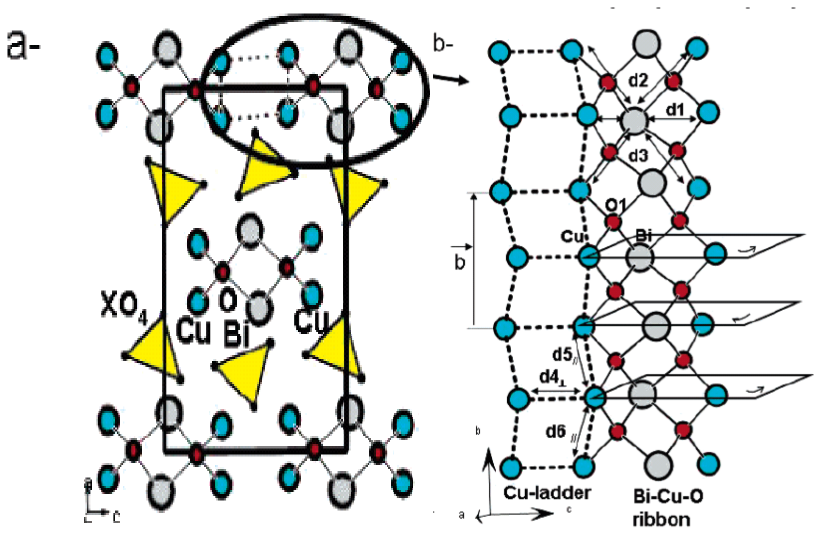


Figure 1.- BiCu2PO6 crystal structure.[2]

Figure (2) shows its crystal structure and ribbon and ladders along the b axis, dotted lines are Cu2+ zigzag ladders. [5]



2.2. The effect of Zn impurity in structure:

In this spin ladder system, each Cu site has an S=1/2; (Because of the existence of Cu^{+2} which has a single spin in it structure S=1/2); and the interactions among these spins are described by Heisenberg Hamiltonian:

$$H = \sum_{<ij>} JijSiSj \qquad (1)$$

There are 4 different spin coupling in the BCPO structure. First, the interaction along the legs, via corner sharing oxygenO2 that create PO4 and is equal to $J_1/k_\beta = (80+2)$ K. Second the rung coupling J_2 via the edge-sharing oxygen O2. The ratio of the interaction along the rungs to the interaction along the legs, J_2/J_1 , is close to 1 So it can be considered as an isotropic ladder.(Because this value is more than 0, it is a good prove for the existence of a Spin-Gap in its excitation spectrum; $\Delta \sim J_2 - J_1$) Third, the NNN coupling along the leg is called J_4 and is about 0.3 J1. Forth, there is an interaction between ladder via Bi element, which is about $J_3 = 0.74\, J_1$.

At the ground state, spin-pairs around the rungs are locked in to the singlet. By introducing Zn as an impurity at the Cu site one of these paired spins are removed and put the other un-paired. As a result, for each Zn, a spin equal to 1/2, S=1/2 ,is released, but in the experiment this number is less than expectation and is about 0.35-0.45 and it refers to the frustration effect due to the NNN (next nearest neighbors') interaction along the leg, because of its zigzag shape. These released spins are not localized and extend as an induced magnetic cloud along the leg. But at enough low temperature, below the Tg, this cloud is localized in a region, with the size of the ε, around the Zn and leads to a spin freezing in the crystal, in such a condition the spins are distributed randomly, and as a result the crystal is changed from the spin-gap to gap less one. The extension of the cloud depends on the percentage of the impurity and in the cases of less impurity in order of 0.1%, according to the result of NMR (Nuclear magnetic resonance), it doesn't extend more than 50 cells.

µSR is another way which is used to prove the extension of the magnetic cloud for each impurity is limited to just few units around it. one can find more details in [3,4].

3. Calorimetric methods:

In this experiment we used the temperature-modulated calorimetry, TMC or in brief AC calorimetry. This method for the first time was presented by F.Sullivant and G.Seidel in 1968 [6] and at the same time by Handler et al although the first specific heat measurement refers to Corbino in 1910. This classical method is actually useful in studying the small samples for all temperature. Further this method extended to Chemical reaction method, $100<T<2000$K, differential scanning calorimetry, DSC and temperature-modulated scanning calorimetry, TMSC which verifies not only the temperature but also its frequency dependence.[1]

3.1. Basic of AC Calorimetry:

In Ac calorimetry, the sample is heated by a periodic power with frequency equal to 2 ω ($P=TR^2$). As output, the oscillating temperature, T_{AC} will be recorded as a function of time. Because of the finite thermal conductivity between sample and sample holder and its surrounding, on the other word because of the resistance of the sample and sample holder and other things in its surrounding that cannot be ignored, a phase shift ,Φ appears between T_{AC} and applied power.

The basic calculations are [1]:

$$I = I_0 \cos \omega t \qquad (2)$$

$$P(t) = C_s\left(\frac{dT}{dt}\right) + K_B(T_s - T_B\,), \quad (3)$$

$$T_s = temperature\ of\ sample\ and\ T_B = bath'stemperature.$$

$$P(t) = \mathrm{P_{AC}}\,\mathrm{e}^{\mathrm{i}2\omega} = 2\mathrm{i}\omega\mathrm{C_s}\Delta\mathrm{T}^*(\mathrm{t})\mathrm{e}^{2\mathrm{i}\omega} + \mathrm{K_B}\Delta\mathrm{T}^*(\mathrm{t})\mathrm{e}^{2\mathrm{i}\omega} \quad (4)$$

$$\Delta T_{AC} = \Delta\mathrm{T}^*\mathrm{e}^{\mathrm{i}\omega} = |\Delta\mathrm{T}^*|\mathrm{e}^{\mathrm{i}\emptyset}\mathrm{e}^{\mathrm{i}\omega} \quad (5)$$

In this equation ΔT_{AC} is amplitude of the oscillation around mean temperature.

By considering the specific heat as a complex number after some calculation, one can find:

$$C_s^* = C' - iC'' \quad (6)$$

$$C' = -\left(\frac{\mathrm{P_{AC}}}{2\omega|\Delta\mathrm{T}^*|}\right)\sin\emptyset \quad (7)$$

$$C'' = \left(\frac{\mathrm{P_{AC}}}{2\mathrm{w}|\Delta\mathrm{T}^*|}\right)\cos\emptyset - \frac{\mathrm{C}}{2\omega} \quad (8)$$

$$|\Delta\mathrm{T}^*| = \frac{\mathrm{P_{AC}}}{[(2\omega\mathrm{C_s})^2 + \mathrm{K_B^2}]^{\frac{1}{2}}}\ , K_B = \left[\frac{\mathrm{P_{AC}}}{|\Delta\mathrm{T}^*|}\right]\cos\emptyset\,, \text{and } \emptyset = \arctan\left\{\frac{2\omega\mathrm{C_s}}{\mathrm{K_B}}\right\} \quad (9)$$

The imaginary part of specific heat appears because dynamic specific heat is measured. Normally imaginary part refers to dissipation process while about specific heat it cannot be a reasonable interpretation, because heat doesn't transform to any other form of energy.

For canceling this imaginary part and simplifying the calculations, we can choose the thermal resistance of bath, RB is much larger than the sample's heat capacity; RB>>Cs, so the phase shift will become Φ=л/2, and the ΔT_{AC} will be reduced to $\Delta T_{AC}=P_{AC}/\omega C$.

Besides, there is a shift in $\Delta T_{AC,}$ and as a result in specific heat, due to the existence of DC voltage in applied power. This shift is given by:

$$\Delta T_{DC} = \frac{P_{AC}R_B}{2} \quad (10)$$

So the total temperature will be:

$$\Delta T = \Delta T_{AC} + \Delta T_{DC} \quad (11)$$

The abbreviation of this calculation which is the basis of our calculation in this experiment is:

$$\Delta T = \frac{1}{i\omega C + k} \quad (12)$$

$$|\Delta T| = \frac{1}{(\omega^2 C^2 + K^2)^{1/2}}\ , K = K_s + K_{wires} + K_{bath} \quad (13)$$

By ignoring the K in comparison with ωC, this calculation will become: $\Delta T = P_{AC}/\omega C$.

Because the voltage between the bath and sample is the parameter which is measured, by using the thermocouple table, Sv, one can change this parameter to ΔT:

$$\Delta T = \frac{\Delta V}{Sv} \quad (14)$$

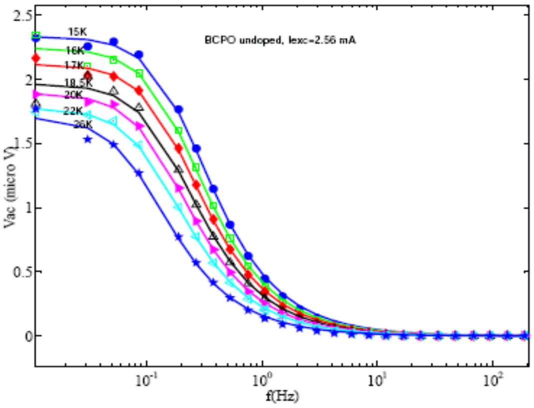
This relation is true either for alternative temperature or for DC temperature.

3.2. Proper frequency:

The frequency which is applied for the temperature scanning of the specific heat is actually important. There are some different ways for choosing the proper applied frequency. For example by considering the relaxation time Τ, the time which is needed that sample arrives to a thermal equilibrium, this frequency can be chosen. For explanation and details can be found in reference [7].

But in this experiment for avoiding of entering the effect of Τ, we did a frequency scan over the sample in three different temperatures for each one. At very low frequency Cp becomes irrelevant and according to the equation (13), temperature gradient, ΔT, depends just on K. On the other hand at very high frequency, the heat loss from bath to the sample can be neglected, but the ΔT will become very small and we can't get appropriate result for Cp. As a result the best frequency should be chosen above the cross over; $\omega>\omega_{cut}$. This is perfectly shown in figure 3 for un-doped sample. So by drawing the plot of Vac as a function of ω, in the logarithmic scale, the best frequency will be in the region in which by variation of frequency, Vac remains unchanged Figure (5).

For un-doped sample, this frequency scanning were done in T=15, 16, 17, 18.5, 20, 22, 26 K, and for the doped one, the chosen T for this scanning were, T= 5, 6, 15. In both cases the chosen frequency which was used for temperature scanning was, ω=3.1.



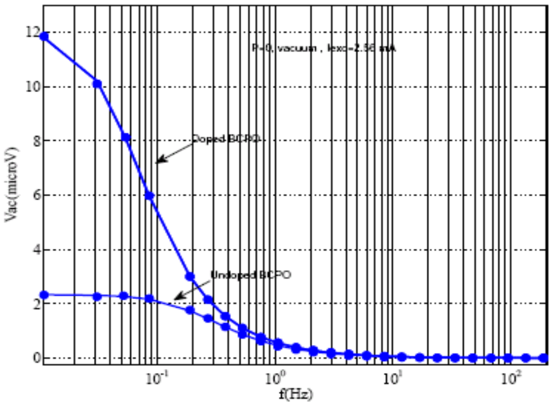


Figure3- Vac Vs ω for different T,un-doped sample. Figure4- comparison of Vac Vs ω for both sample

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4. Setup of experiment:

4.1. preparation of the sample:

After polishing both sample, we put them in the acetone and in ultrasonic bath for 30 min. So for having a better connection on the surface of the sample, a thin layer of Platinum, 20 nm, Pt, was deposited on it, in the way that the sample is divided in two separate parts with an insulating line between them.

For the un-doped sample, in one part 4 wires of Mn with the diameter of 0.025 milli-meter were attached to the sample, via silver paint DUPONT 4929N, (suitable for electrical transport measurement), 2 for measuring the voltage and 2 for current and heating the sample, and both for finding the resistivity of the Pt layer. In the other side one thermocouple of Au -0.07At%Fe and Chromel, with the thickness of 0.025 mm, was connected to the surface by using the Silver epoxy H31LV, (suitable for thermodynamics measurement), figure (5). But in the doped one, just two Mn wires for sending the current, were attached, because there was no more need to measure the Pt resistivity, it has the same temperature dependence like un-doped sample. This time, on the second part, 2 different thermocouples were connected, Au -0.07At%Fe and Chromel, which has a good sensitivity for the Temperature below 40K, and the second one Chromel and constantan with sensitivity for the temperature between40 and 80K, because we wanted to measure the Cp in wider range of temperature.

It this part of the experiment we didn't use the second thermocouple, because we did the measurement up to 40 k.

One of the most important things for both thermocouples is that both wires should have connection together and to the surface just in one point.

The best way for curing the via silver paint DUPONT 4929N, is either put the sample in to a pre-heated oven for 50-60 min at 70-75 or 40 min at 90-100 C, never higher than 100 C, or at room temperature for 14 h. and for the Silver epoxy H31LV, the best way for curing is putting it in a Aluminum foil , then put it in to the pre-heated oven at 150 C for 1 h, or at 80 C for 8 h, in the second way the change of having a successful curing decreases at least 30%.

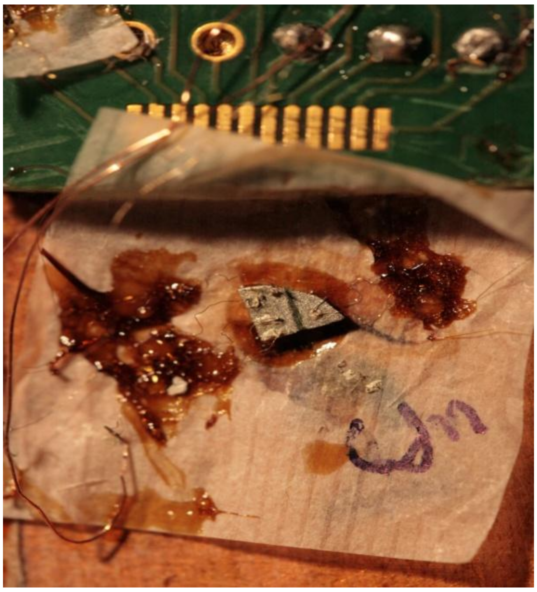


Figure 5- un doped sample with attached wires on its surface.

4.2. Preparation of sample holder:

The sample holder in this experiment is made of copper, which has good thermal and electrical conductivity. Figure (6) shows a schematic shape of this holder. Wires pass through the cylinder part, and from the top are connected to the pasted sample, and in the bottom are connected to AC Calorimeter (the setup the experiment).

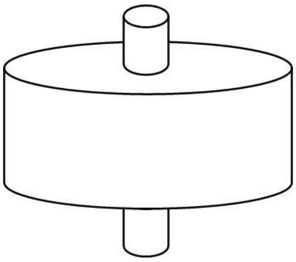


Figure 6- Schematic picture of sample-holder.

Inside the holder was filled with Black Stycast, solved in the catalysis 9, for having a good chemical resistance and physical strength. Amount of the catalysis 9 per 100 part of Stycast is 3.5 by weight or 8.5 by volume. After filling out the hole of sample holder with this mixture, we put it in the oven in 80°C for 8 hours.

Sample is attached to it by its wires. Figure (7) shows a picture of the attached sample to sample holder.

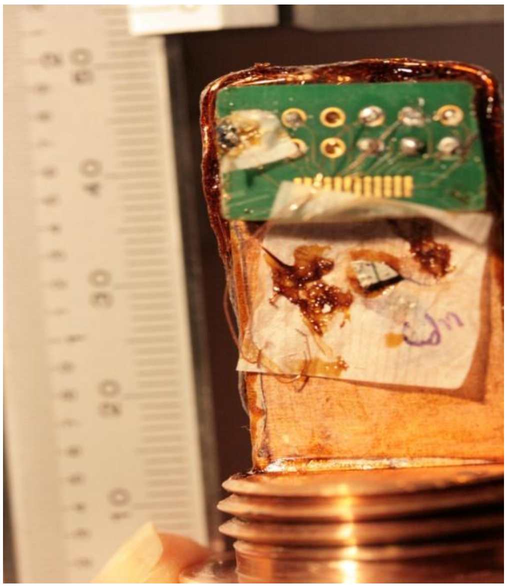


Figure 7- sample attached to the holder.

4.3. Preparation of the AC calorimeter:

Because we want to do our measurement in the pressure equal to zero, P=0, we pump the setup. Another reason of using the pump is thermally isolating the system from its surrounding to be able to control its temperature. For this purpose, we connect a turbo pump to the measurement system. Besides, because the measurement is carried out in low temperature, from 3 to 40 K, the sample should be kept in a helium reservoir; temperature of the measurement can be changed by AC Calorimeter. Figure (8) shows the experiment's set up.

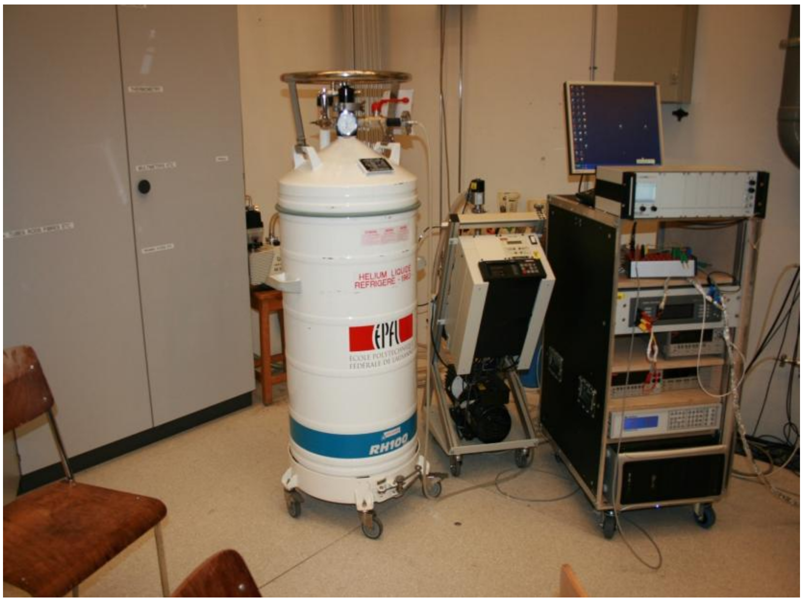


Figure 8- Calorimeter, helium reservoir and turbo pump.

5. Measurement:

5.1. The platinum electrical resistance:

For finding the Rs, or the resistance of Pt, we applied a Current of 100 μA trough two Mn wires, at temperature 24.5K, and collected the data in the form of voltage from other two wires. This configuration is known as of 4 point probe s method or 4-terminal sensing. This method is more accurate than 2-terminal sensing, because it doesn't take into account the voltage drop due to the effect of the wires 'resistance. Pt Resistance below 20K is constant; in fact it changes less than 1 percent from 20 K down to 4K. So we can assume that resistance is also constant at T= 24.5 K, without any frequency dependence. As a result we did our measurement with the DC current Not Ac.

We need this resistance to be able to calculate the applied power from the applied current from equation:

$$P = RI^2$$

Figure (9) shows the resistance of Pt as a function of T for un-doped sample. And figure (10) shows this resistance for Zn doped ample.

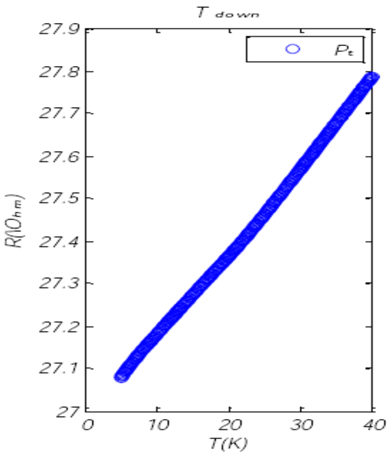


Figure 9- Pt resistance Vs T un-doped sample.

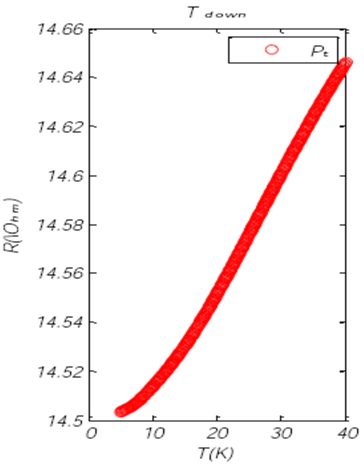


figure 10 – Pt resistance Vs T Zn-doped.

5.2. Tdc the Dc part of voltage (V_{dc}):

The average power creates a dc shift upwards in temperature ΔTdc. This leads to a component Vdc in addition to Vac which creates a shift in specific heat. This shift can be measured easily. as it is explained in theory in section (3.1). V_{dc} usually has to be measure separately for each sample. But in our case because we use the same excitation current, the temperature dependence should be the same, but there is likely a scaling factor between them. But because the effect of this part is very small, and almost nothing in our calculations, we considered the same value for both of them.

The excitation current which was applied in our measurement was:

Iex= 2.56 mA, for un-doped sample and Iex=2.56 mA for Zn-doped one.

In this measurement for calculating the ΔTdc due to the V_{dc}, we used a smooth Vdc offset in matlab programming. Figure 11 shows the Vac versus T, and figure 12 shows Tdc versus T.

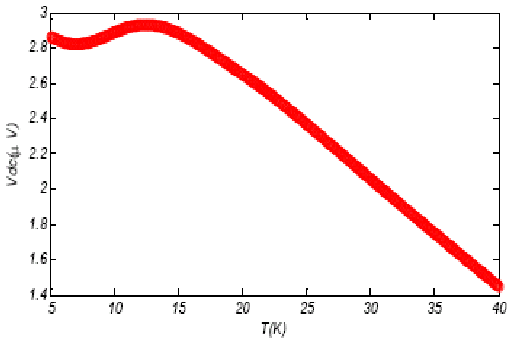


Figure 11- Vdc versus T. for both sample.

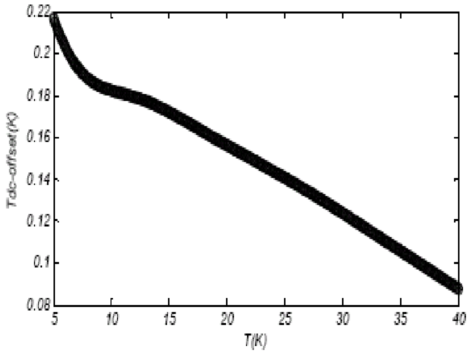


Figure 12- Tdc versus T. for both sample.

5.3. F-scanning the sample:

As I explained in section 3.2, for finding the proper frequency in which we measure Cp as a function of T, we use F-scanning for some chosen temperatures. The frequency which was selected for both samples in this way was 3.1HZ.

5.4. T-scanning the sample:

After finding the appropriate frequency, the final step is finding the specific heat of both samples as a function of temperature. For this, we did the measurement for the temperature from 3 to 40 K. figure (13) shows the Vac Vs Tac for un-doped sample, and figure (14) shows the same plot for Zn-doped one. As we see there exist no matching data, or maybe some missing data for this case.

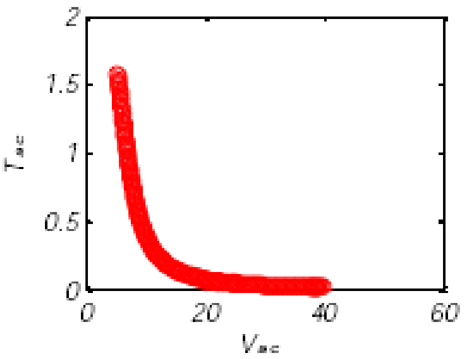


Figure 13- Vac Vs Tac for un-doped sample.

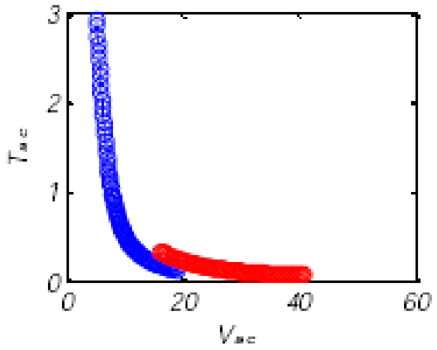
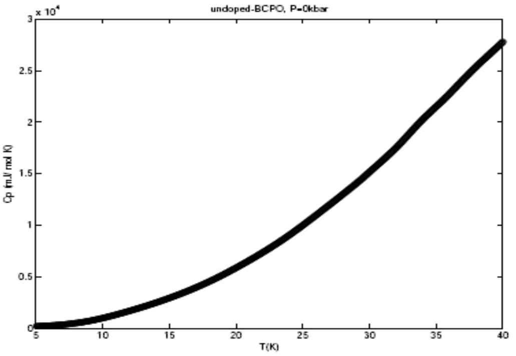


Figure 14- Vac Vs Tac for Zn-doped sample.

Figure (15) shows the Cp of the un-doped sample as a function of T. Figure (16) refers to the same measurement for the doped sample.



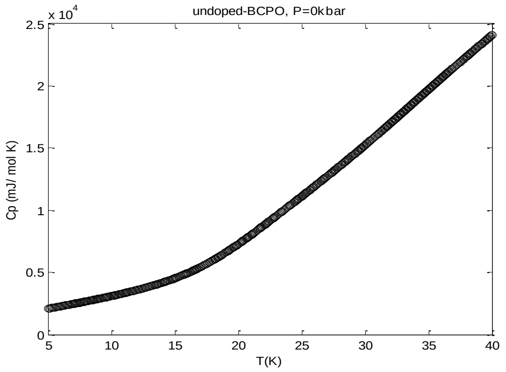


Figure 15 – Cp for un-doped sample as a function of T.

Figure 16- Cp for Zn Doped sample as a function of T.

6. Conclusion:

1. The un-doped data agree (qualitatively or even quantitatively) with literature results. [2]
2. The total specific heat contains a phonon part, which one can try to describe by a so-called Debye model, and a magnetic part, which should reflect the spin gap. One can find more details in [4]
3. The doped data is different. Based on low doping level in the sample, x=0.01, according to [2], there should be very small different and almost nothing in the result. Consistency check of the measurement and analysis is needed to determine if this is real or an artifact of the measurement/analysis. For example Pt resistance in doped sample in smaller that un-doped one, figures (9) and (10) , or it may refers to un matching, or maybe missing data regarding to figure (14).

Once we are able to compare the two samples, the difference should be related to the physics presented in chapter 2.

Outlook:

The next part of this experiment that will be done in future semester should be done between BiCu2PO6 while it has no impurity and while its Cu has been replaced completely by Zn while a high pressure is applied.

To be done:

1. Consistency checking the doped measurement/analysis. If necessary redo the measurement.
2. Measure sample with all Cu replaced by Zn. That sample will be non-magnetic and hence only have the phonon contribution. This can then be used as background to subtract and obtain the magnetic contribution in un-doped and lightly Zn-doped samples.
3. Measure under pressure. Firstly we should just measure the pure compound to see if the spin gap changes under pressure.

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TP4 project report

Saba Zabihzadeh

Supervisors: Henrik M. Ronnow

June 2010

1) Introduction:

This report is the summary of what has been done for my TP4 project in second semester at "laboratory of quantum magnetism (LQM)" under the supervision Prof.H.Ronnow. This project is the continuation of first semester regarding to measurement of specific heat of BCPO. The subject is to measure and compare the specific heat of two samples, BiCu2PO6 and BiZn2PO6 under applying pressure. This comparison leads to understanding the change in magnetic structure of BCPO, which has Spin-Gap, after replacing its Cu ion with non-magnet element Zn. Zn has no magnetic momentum, so its specific heat behavior is a good approximation of phonon interaction part of BCPO, and by subtracting this part, we can find the magnetic behavior of BCPO.

One can find more information about crystal structure, on reference [1].

For measuring Cp, we again used AC-Calorimetry method, which is based on heating up the sample via an AC current.

2) Preparation of Sample:

Because both samples should be put together inside pressure cell, we reduce their size to following dimension:
2.0(-5) mm x 2.0(-5) mm (surface) and 0.20(-5) mm thickness.

If the thickness of both samples were the same, we could use the same frequency in our method. But unfortunately, we had to change one of our samples and the BZPO one became thicker. After polishing these samples, we put them in acetone and ultrasonic bath for around 1 hour, and put them in the air for 1 hour to let them dry. Afterward, we sputtered Pt film with thickness 20 nm on the polished surface. It is very important that Pt adhere to both samples very well. At the end, each surface should be divided in two parts without any electrical connection with each other.

3) Wires connection on sample surface:

To measure the temperature change of samples due to passing AC current, we put a thermocouple of Au -0.07At%Fe and Chromel, with the thickness of 0.025 mm, on one part of each surface. To fix the connections, Silver epoxy H31LV, suitable for thermodynamics measurement was used. 2 wires of Au -0.07At%Fe, which has very low electrical and thermal resistivity, are attached on the second part of each surface to measure the voltage of Pt resistance. Current was sent by magnesium wires to both samples in series way. This configuration is called as 4 points probe method or 4-terminal sensing. This method is more accurate than 2-terminal sensing, because it doesn't take into account the voltage drop due to the effect of the wires 'resistance.

Both samples with their connected wires are attached to a surface. On the other side of this surface, a pure lead is attached. We tried to increase its resistance by reducing its thickness and increasing its length. Its resistance is measured via 4 attached copper wires to its surface.

4) Obturator with wires feedthrough:

Samples are fixed on a piston which goes through pressure cell. This piston is a commercial Russian product made of NiCrAl; CuBe is a substitute material which can be used to make this piston.

16 twisted wires are pass through it, afterward it is filled with stycast epoxy (Stycast 2850 FT) to avoid a leak of the pressure medium. For having a good chemical resistance and physical strength, stycast, is solved in the catalysis 9, with the ratio of 9 per 100 part of Stycast, 3.5 by weight or 8.5 by volume. After filling out the holder with this mixture, we put it in the oven in 80°C for 8 hours to be cured.

5) Working with Pressure cell:

The pressure cell used in this experiment is CC33 pressure cell, a commercial Russian cell made of beryllium-copper in outside and Ni-Cr-Al in inner cylinder.
BeCu is a non-magnet material with a high strength over wide range of temperatures, and good thermal conductivity. Figure (1) shows different parts of this cell.

Figure 1. main construction of the CC33 nonmagnetic optical pressure Cell, 1 - Body, 2 - Piston, 3-Obturator, 4 - Screw for piston, 5 - Screw for obturator, 6 - Push rod. [2]

One can find more information about this commercial pressure cell and a copy one which has been made in IPMC "institute of condensed material in physics" in reference [2].

5.1) Applying pressure on cell:

Before putting our samples inside the cell and applying pressure, we put our samples inside a Teflon tube, with Yield strength 23Mpa, to seals the cell, in this way the pressure medium does not leak out.

Moreover, to avoid any air-bubbles inside the tube, we put the sample inside the Teflon tube while it is immersed in the oil. If there remain some bubbles inside the system, during pushing the piston, they collapse and don't let the inside pressure increases. In fact, air-bubbles limit applied pressure.

There is a relation between applied pressure, which is displayed on press, and pressure inside the cell. There is a calibration curve in reference [2] which shows this certain correspondence. But in our case, we use variation in lead superconductivity transition point to measure the exact value of applied pressure.

5.2)Calculation of applied pressure:

Superconductivity transition point of lead happens in lower temperature while it is under pressure. There is a function which describes the change of lead's transition point or superconductivity temperature as a result of applied pressure. Equation (1) shows this relation:

$$P = \frac{T_c(0) - T_c(P)}{0.365 \pm 0.003}\ [GPa] \qquad (1)$$

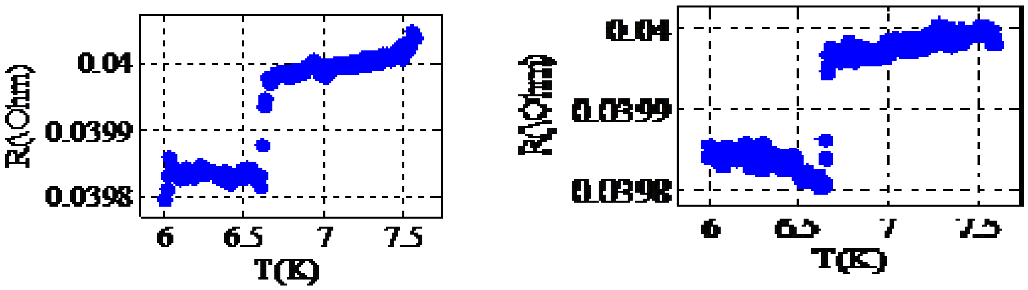
Lead superconductivity temperature at ambient pressure is around Tc= 7.12 K. To find this temperature while system is under pressure, we did the measurement several times and tried to take an average in our obtained data.

In below, we have put our plots in different measurement.

Due to temperature gradient, we measured resistance of lead for both cases of increasing and decreasing temperature.

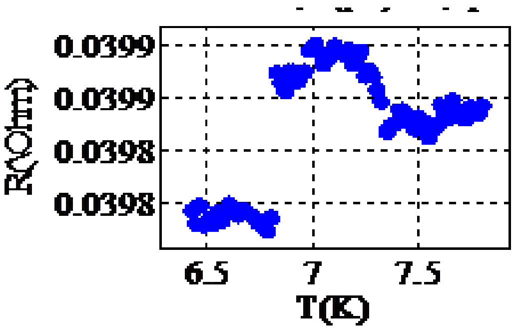
Figure (2)

Data on lead transition temperature while it is under pressure, a, c and e are result for increasing temperature, b and d ar edata for decreasing temperature.

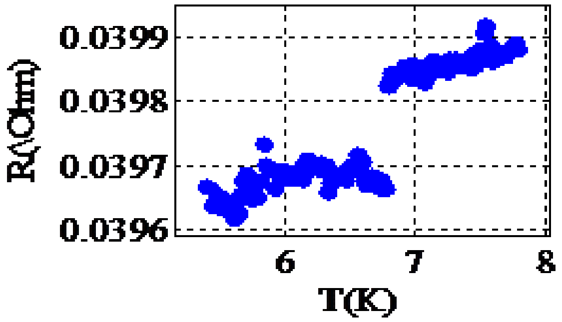


a. Increasing T, Tc=6.6

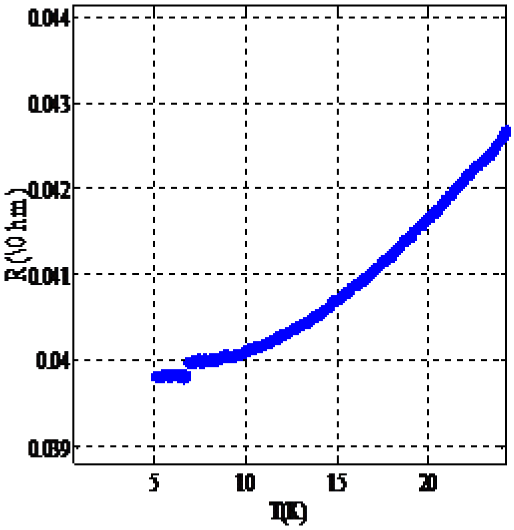
b. Decreasing T, Tc=6.64



c. Increasing T, Tc=6.8



d. Decreasing T, Tc=6.76



e. Increasing T, Tc=6.799

If we take and average among our obtained data, we found the critical temperature Tc=6.72K. lead transition point in ambient pressure is Tc=7.12K, so according to equation(1), applied pressure will be equal to 1.1 Gpa.

6) AC Calorimetry method:

For calculating specific heat of our samples we used the temperature-modulated calorimetry, TMC or in brief AC calorimetry. In Ac calorimetry, the sample is heated by a periodic power with frequency equal to 2 ω ($P=TR^2$). As output, the oscillating temperature, T_{AC} will be recorded as a function of time. The final equation which is used to measure Cp, specific heat in this method is as below:

$$\Delta T = \frac{Pac}{i\omega C + k} \qquad (2)$$

$$|\Delta T| = \frac{P_{AC}}{(\omega^2 C^2 + K^2)^{1/2}}\ , K = K_s + K_{wires} + K_{bath} \qquad (3)$$

In which P_{AC} is applied power, $P=RI^2$, and ΔT is calculated as:

$$\Delta T = \frac{\Delta V}{Sv} \qquad (4)$$

Sv can be read from thermocouple table for Au -0.07At%Fe and Chromel thermocouple.

It should be mentioned that here is a shift in ΔT_{AC} due to the existence of DC voltage in applied power. So our ΔT has two parts: $\Delta T = \Delta Tac + \Delta Tdc$.

More explanation can be found in reference [1].

In this experiment we use Lock-in Amplifier, Model 7265, Lake shore, temperature controller, Model 340.

7) Measuring applied power:

In general case, applied power is calculated as a function of excitation current and plutonium film resistance.

$$\mathbf{P=I_{exc}^{2}*R_{Pt}} \quad \mathbf{(5)}$$

We can consider two different situations:

1) Constant power, P_0. In this case specific heat has dependence on measured voltage in Lock-in.

$$\mathbf{C \sim P_0/Vac(T)}$$

2) When power changes as a function of temperature. $P_0(T)$

$$\mathbf{C \sim P_0(T)/Vac(T)}$$

In these equations, Iexc is heat up current which is applied to Pt film via Lock-in.

8) Measurement of excitation or heat up current :

In general excitation current is determined by following relation:

$$Iexc = \frac{Vexc}{Rl + Rs + Rwires} \qquad (7)$$

Vexc=Vosc, is heat up voltage which is defined by us due to experiment's conditions.

Rl= resistance of Lock-in =50 Ω

Rs=sample resistance=Rpt(BCPO)+RPt(BZPO)

R (wires)= resistance of all wires coming from sample+ R (magnesium) + R(soldering)+R(Cu)

Because resistance of wires and Plutonium film have metallic behavior by temperature; it means their resistance increase by rising temperature, due to the constant excitation voltage, which we have defined it in Lock-in at the begging of experiment, one should expect a decreasing in Iexc for temperature above 15K, (below this temperature resistance and as a result excitation current can be considered constant.)

Excitation current can be measured by putting a 1 Ω resistance in series on the way of heating current of Lock-in. In this configuration, measured voltage through this resistance via Lock-in, would be equal to excitation current. This configuration is drawn schematically in figure (3).

Iexc=Vtest/1Ω (6)

Vtest is the measured voltage via Lock-in in our configuration.

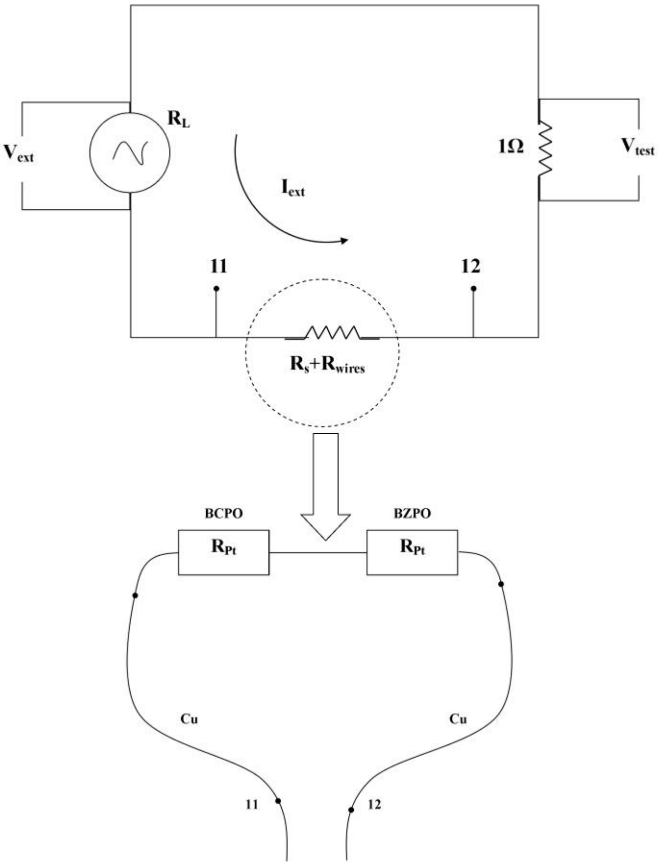


Figure (3), schematic configuration of Vexc measurement. In this figure Rl is the resistance of Lock-in, Rpt is platinum resistance of samples and R(wires) is resistance of all wires contain resistance of soldering. 11, and 12 are the wires which connect to heater of Lock-in, excitation current pass through these wires, and V(test) is measured by Lock-in.

As it was explained before, this current decreases above 15 K. To have a constant excitation current, we have to increase excitation voltage above 15 K in our system.

For calculating excitation voltage, we chose Vosc, or Vexc, in Lock-in at the beginning 1milivolt. Then we took 12 different temperatures in the range of 5 to 70K, and we did a T-scan of our excitation current. Due to existence of the 1 Ω resistance on the way of excitation voltage, measured voltage, V (test), is equal to the current, and this measurement gives us Pt resistance for different temperatures. Because our excitation current has been selected 3 mA, and we want to keep it constant, excitation voltage for different temperatures is calculated as below:

$$Vexc = 3(mA) * \frac{0.001}{V(measured)} \qquad (8)$$

In this formula, 0,001/V(measured) gives us Pt resistance.

Figure (4) shows our measurement for Iexc and calculated Vexc.

We did T-scan of Iexc for Temperatures: 4.4,10.4,16.4,19.4,22.4,28.4,30.4, 36.4, 40.4,46.6,54.4,60.4,66, 70.4.

V(test)=I(test)=10.73,10.71,10.68,10.67,10.65,10.56,10.51,10.42,10.32,10.22,10.11,9.98,9.86,9.82 (micro volt or micro ampere)

Vexc=0.27966,0.2801,0.2809,0.2812,0.2817,0.2841,0.2854,0.2879,0.2907,0.2935,0.2967,0.3006,0.3043,0.3055(volt)

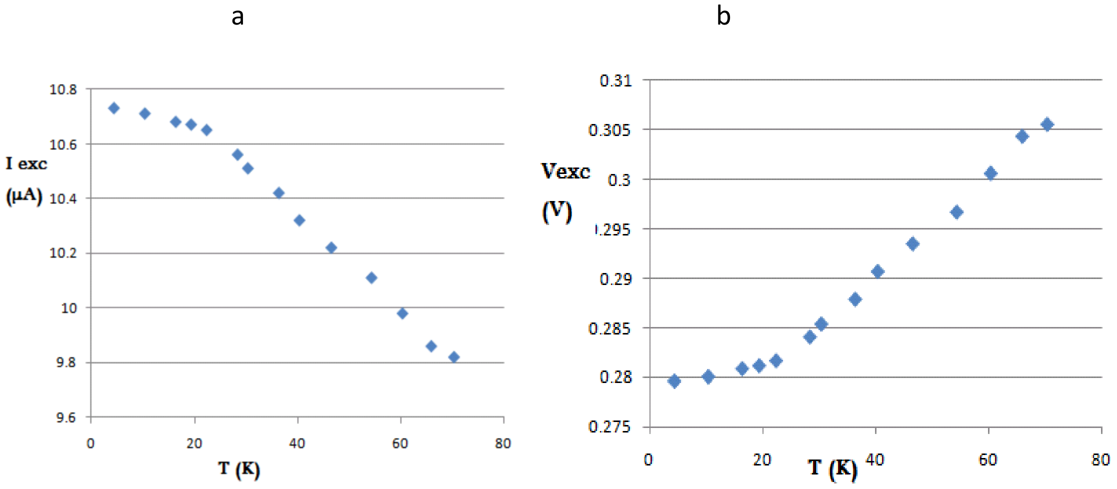


Figure (4) , a) variation of measured excitation current, Iexc, by temperature in constant selected voltage. b) Calculated excitation voltage,Vexc=Vosc, for different temperature range in a constant current

We increased our excitation voltage for higher temperature range based on figure (4), to have a constant excitation current, 3mA.

In this measurement we didn't concern about the variation of power with temperature and took it constant, but instead we increase excitation voltage for T higher that 15K.

9) Measuring of the Pt film resistance:

To measure resistance of Pt films, we worked on the temperature range between 5 and 50K, while temperature increasing step was selected 0.1K. In fact we did a T-scan of Pt resistance to find its metallic behavior over temperature. Figure (5), and figure (6) show Pt film resistance of both samples.

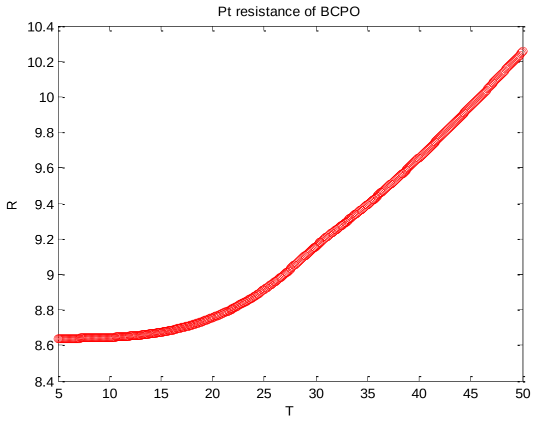


Figure (5) variation of Pt resistance, R (Ω) of BCPO by temperature, T(K)

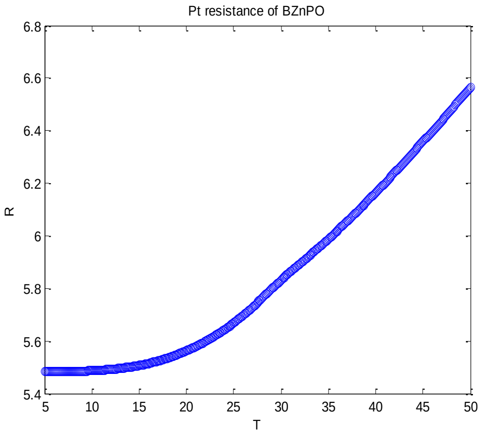


Figure (6) variation of Pt resistance, R (Ω) on BZPO sample by temperature, T(K)

10) Appropriate frequency:

Choosing the best frequency for is one of the most critical point in this measurement. In the best frequency, sample finds enough time to response to passing current. There are different ways to choose the best scanning frequency [1]. In this measurement we did a f-scan of both samples and record measured voltage for each frequency. Figures (7) and (8) show the results of our first measurement.

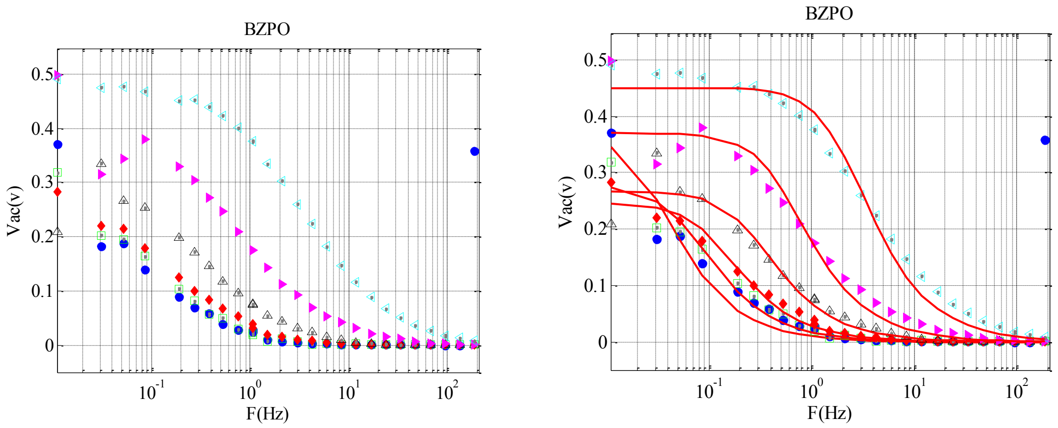


Figure (7), F-scan of BZPO, raw data and fit function

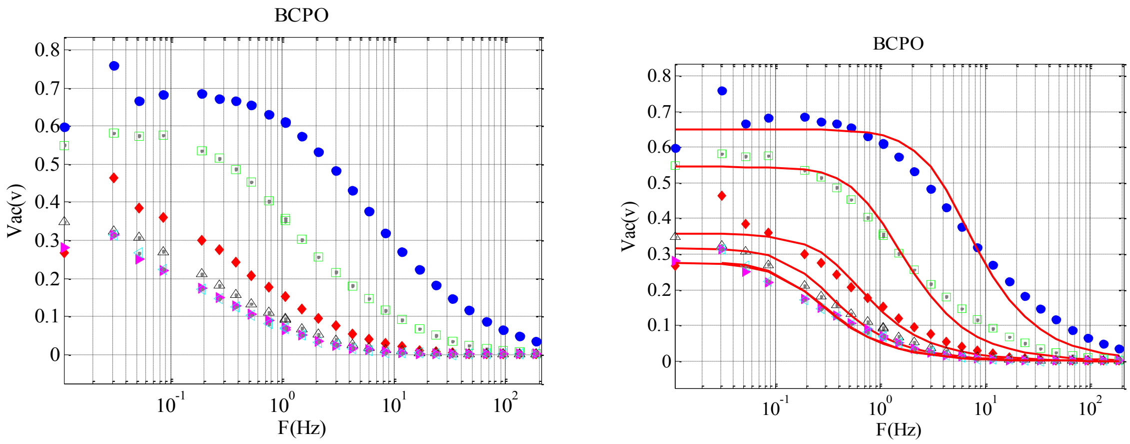


Figure (8), F-scan of BCPO, raw data and fit function

In the first measurement, f-scan was done for T= 5.5, 10, 20, 30, 40, 45, and in the range of [189, 0.0311].

To be sure of our data, we redid the experiment for 3 temperature, T= 5, 20, 40 K. Results are shown in figure (9) and (10).

In second attempt we increased excitation voltage from 0.28 V to 0.54 V, to get less noise. Due to this change, we increase heating power so measured voltage in second f-scan is about 2 times of our first measurement.

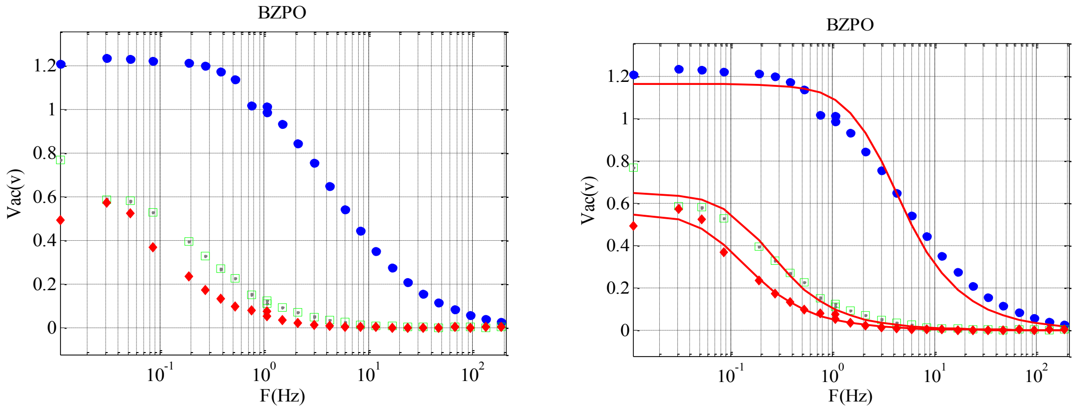


Figure (9), F-scan of BZPO, raw data and fit function

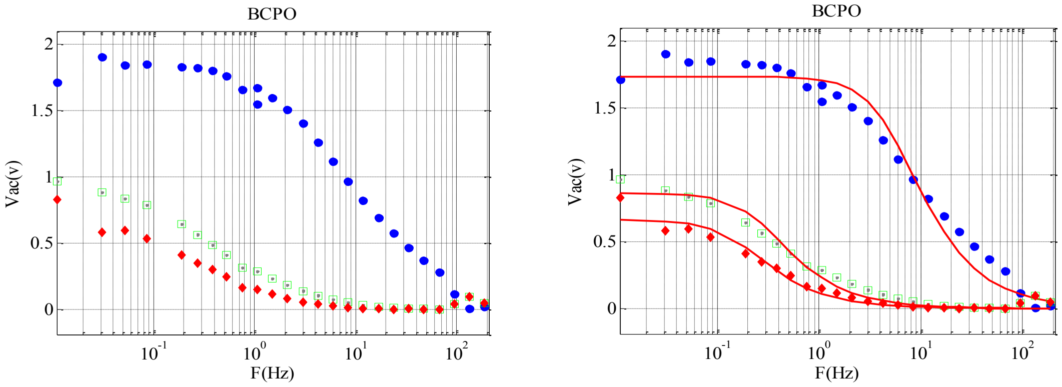


Figure (10), F-scan of BCPO, raw data and fit function

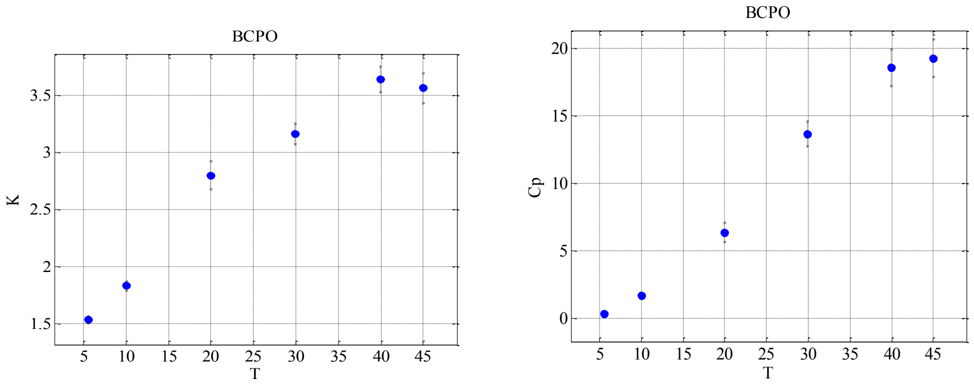
At high frequency, current passes too fast that sample has no feeling, as a result we get zero measured voltage. On the other hand, at low frequency, it is thermal conductivity which plays the most important role in specific heat, equation (2), and measured voltage won't be a suitable one. In the limit of zero frequency, we can ignore ω in equation (2), and as a result Tac depends only on K, thermal conductivity. This parameter is constant for a certain temperature, so we get a rarely constant voltage in our measurement. We can conclude that a frequency in the middle of these two limits can be considered as the appropriate frequency.

Unfortunately, for these two samples, there is a considerable difference in appropriate frequency for temperature below 20K and above that. This makes the selection process quite tricky. As a result, we had to do T-scan of samples for different frequencies and chose the best result.

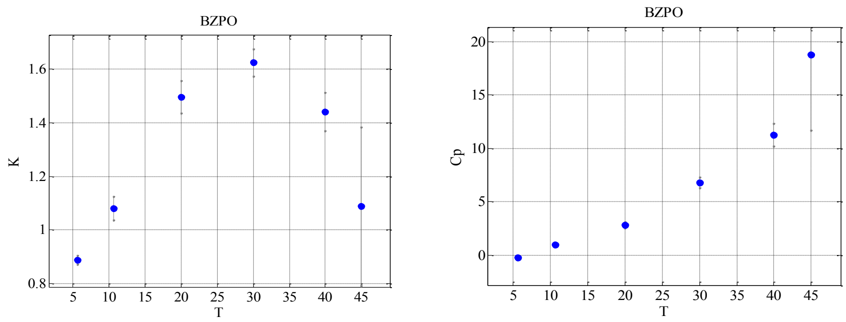
As it is obvious in figure(8) and (10), for temperature below 20K, frequency around 20Hz can be the best one, while for higher T, we should go under 3 or 2 Hz, DC mode, to see a good response from our sample. For second sample, for higher T, frequency around 8 works, while for upper T, we should go around 1 Hz or even smaller one.

Indeed, we have done T-scan of specific heat for BCPO for frequencies equal to 21, 20.4, 8.4, 2.9 and 1.1 Hz. While for BZPO, we selected f=8.4, 3.1, 3.4 and 0.8 Hz. We will discuss about the result of T_scan later.

Measured voltage, or ΔTac, in f-scan, makes it possible to fit obtained data with equation (2) and derive an estimation of the thermal conductivity (K) and specific heat (Cp) of both samples from obtained data in f-scan. For each temperature, we get a point for Cp and k. figure (11) and (12) shows the results of the first f-scan.



Figure(11),variation of BCPO thermal conductivity(W.K^{-1}.A^{-1}) and specific heat(J.Mol^{-1}.K^{-1}) with temperature (K)



Figure(12),variation of BZPO, thermal conductivity(W.K^{-1}.A^{-1}) and specific heat(J.Mol^{-1}.K^{-1}) with temperature(K)

11) T-scan of specific heat for DC-offset:

For measuring the shift due to DC offset in current, we did a T-scan of both samples, while recorded data, voltage, by nano-multimeter (Keithley 2182A). By using thermocouple table for Au -0.07At%Fe and Chromel thermocouple, we transform this measured voltage to ΔTdc, and add to obtained temperature data, ΔTac from AC measurement. Comparison between data from DC data and AC, shows this shift is very small. Figure (13) shows the results.

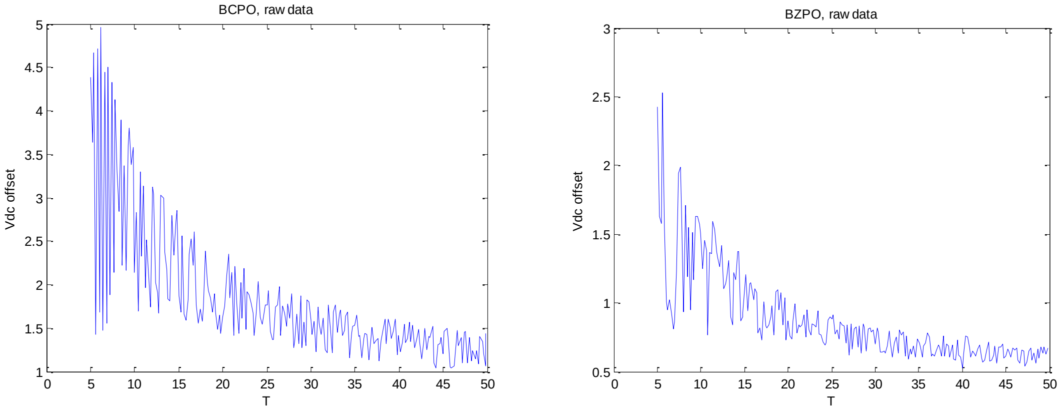


Figure (13), Vdc (V) offset of BCPO and BZPO as a function of temperature(K).

12) T_scanning of specific heat:

Due to the difference in appropriate frequency for different temperature range, we had to select different frequency and redo measurement for each of them to get a favorable plot.

1) In the first try we chose frequency 20.1Hz for BCPO, and 8.4HZ for BZPO, with excitation voltage 0.28. Obtained results for temperature higher than 20K is not acceptable. We got a lot of noises which may refer to non favorable frequency or experiment condition. Figures (14) and (15) show our results.

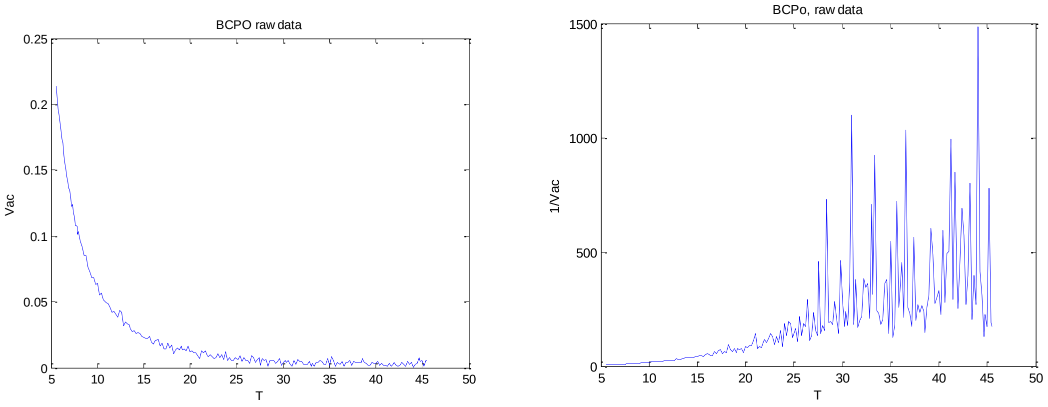


Figure (14), BCPO variation of measured voltage(V) and its inverse by temperature (K), f=20.1 Hz, Vexc=0.28 V

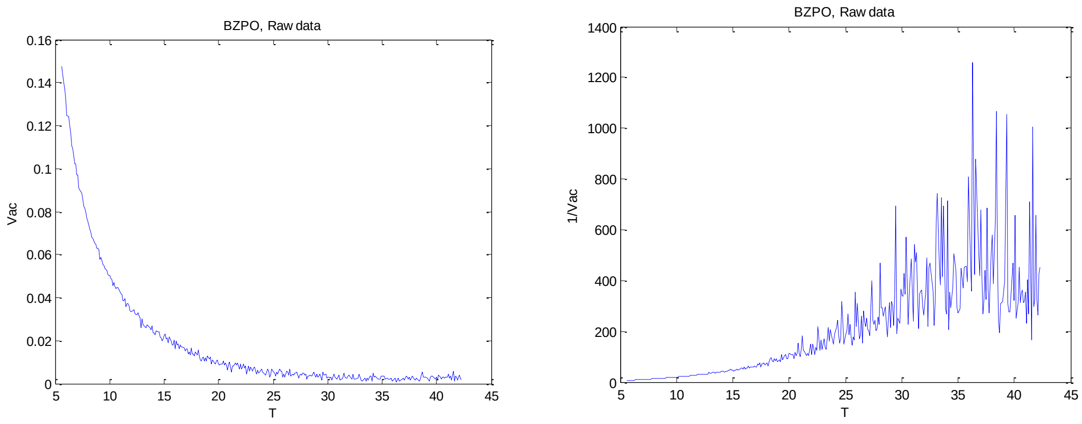


Figure (15), BZPO, variation of measured voltage (V) and its inverse by temperature (K), f=8.4 Hz, Vexc=0.28 V.

2) To find out the source of such an undesirable data and to become sure that these unexpected data refers to noises, we decided to redo the measurement with the same situation. For reducing noise, we chose a higher excitation, heat up, voltage. Figure(16) and (17).

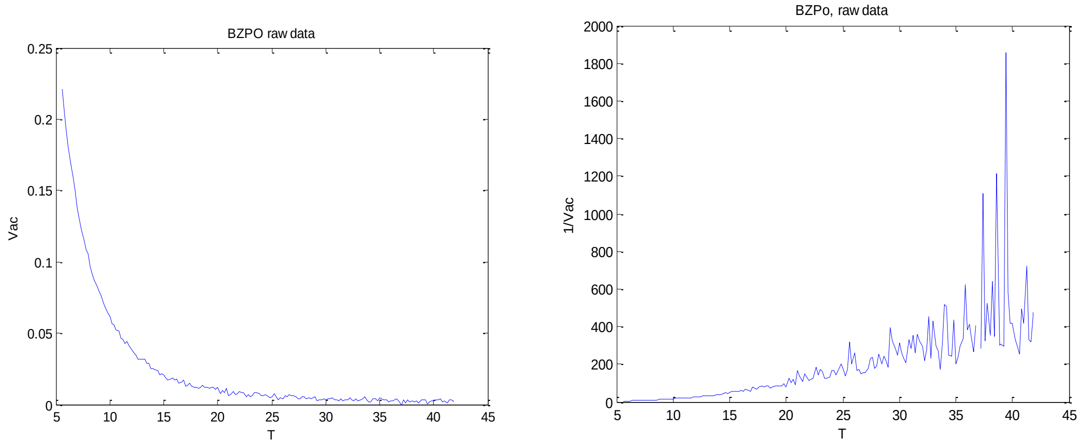
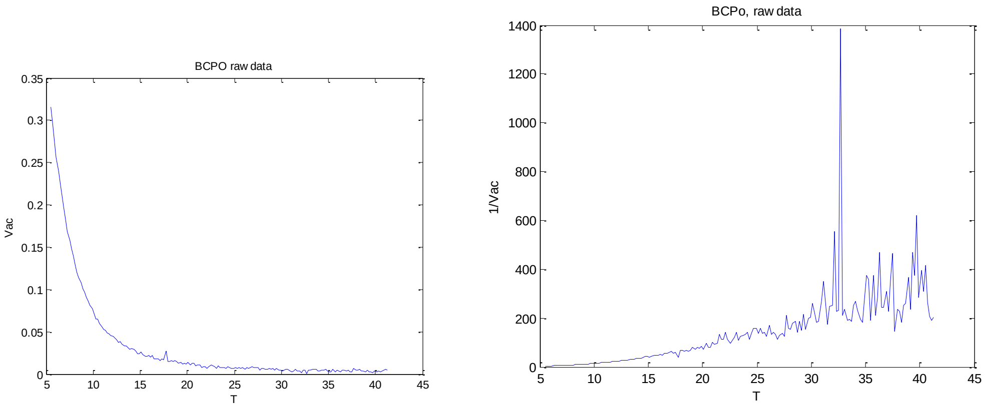
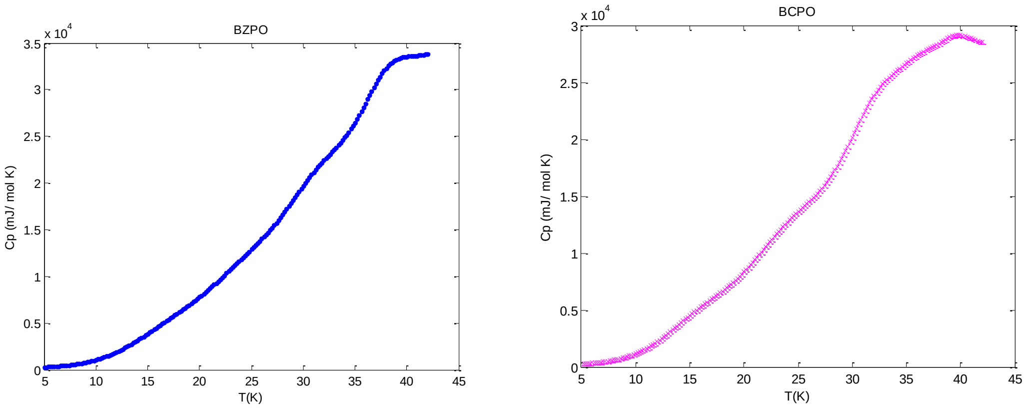


Figure (16), BZPO,variation of measured voltage(V)and its inverse by temperature(K), f=8.4Hz, Vexc=0.34V.



Figure(17), BCPO, variation of measured voltage(V) and its inverse by temperature(K), f=21 Hz, Vexc=0.34 V.

Calculated specific heats based on these measured voltages are plot on figure (18).



a) BCPO b) BZPO

Figure (18), Cp as a function of T. a) BZPO sample (f=8.4 Hz), b) BCPO sample (f=21 Hz), Vexc=0.34V.

To find variation of specific heat with temperature, first we changed Vac to ΔTac by using thermocouple table for Au -0.07At%Fe and Chromel thermocouple, equation (4). After that we put our measured data, concluding resistance of samples and wires, thermal conductivity, selected frequency and ΔTac in equation (2) and plot Cp as a function of temperature.

3) In our third attempt, based on figures (5, 6, 7, 8), we decided to go lower frequency for both samples for temperatures above 20K, below 2 HZ, to find out samples response to this range of frequencies. We only did T-scan of these frequencies for temperatures between 15 and 50. Figures (19) and (20) show the results.

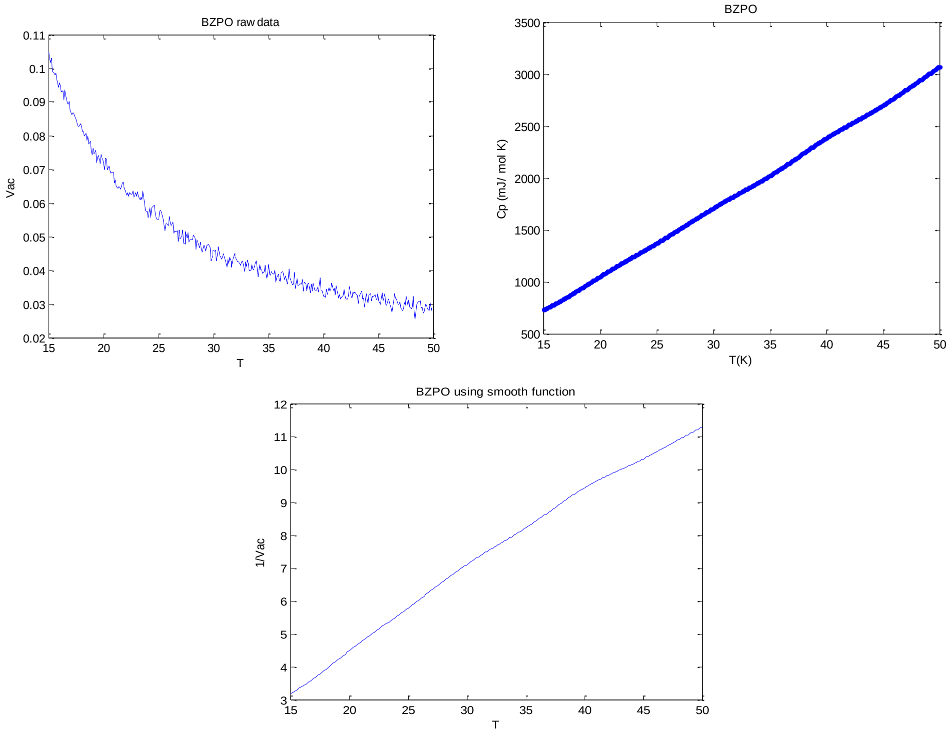


Figure (19), vac,1/vac and Cp plots versus temperaturefor BZPO sample, 15<T<50, f=0.8Hz,Vexc=0.289 V

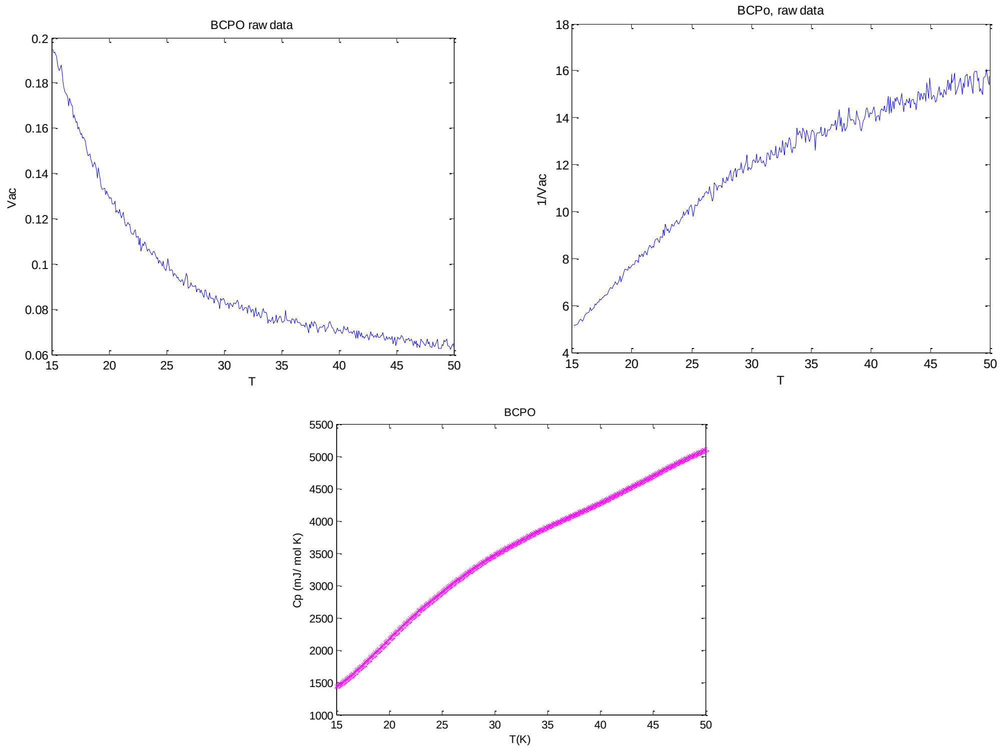


Figure (20), vac,1/vac and Cp plots as a function of temperature for BCPO sample, 15<T<50, f=1.1 Hz Vexc=0.289 V

Although we get almost no noise or out of range data for recorded voltages, but the wrong curvature of our curve proves a wrong selected frequency.

4) In forth attempt, we increase both frequencies to a region around 3 Hz. Figures (21), (22).

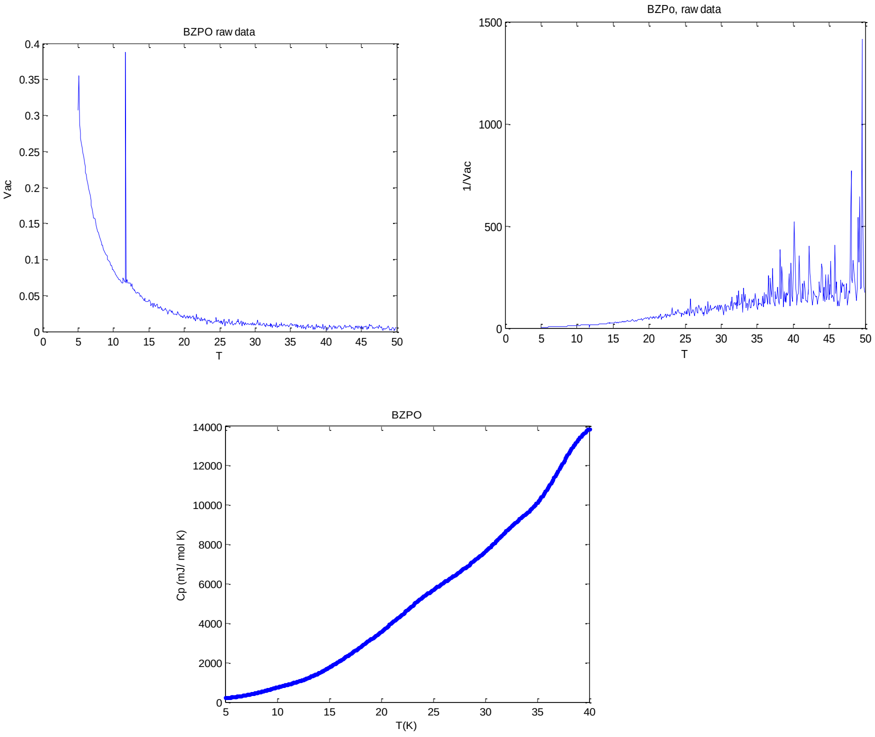


Figure (21), BZPO, variation of a)vac, b)1/vac ,c)Cp with temperature,5<T<50, f=3.1 Hz,Vexc=0.289 V

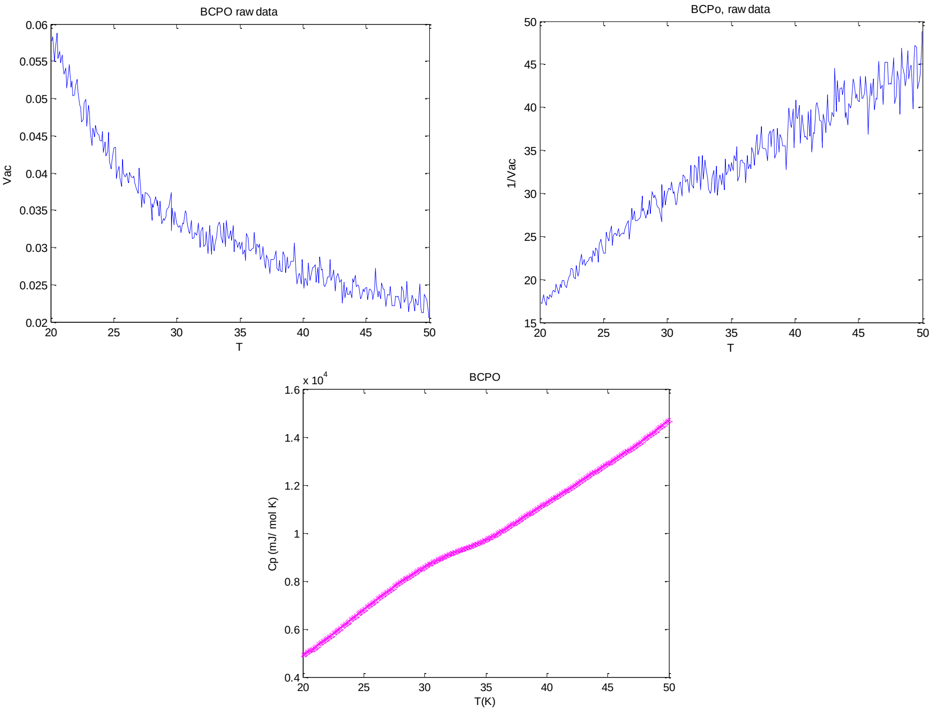
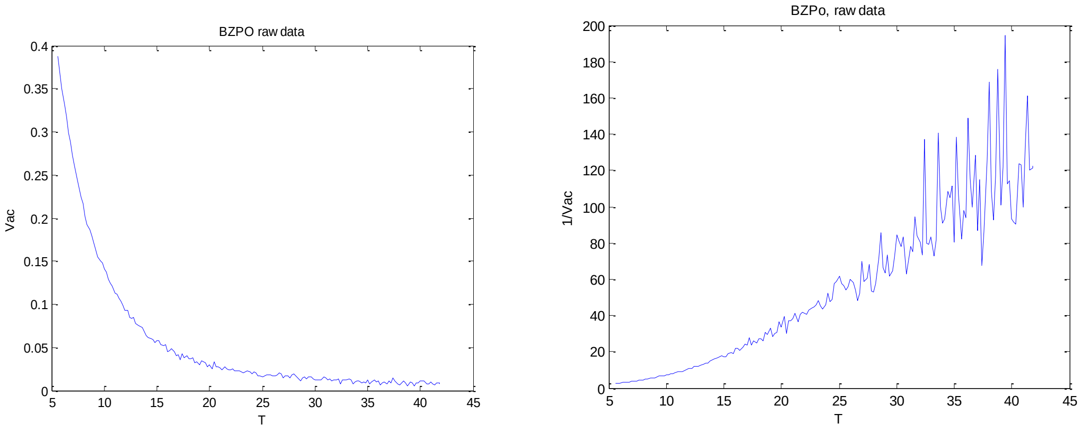


Figure (22), variation of a)vac, b) 1/vac, c) Cp with temperature for BCPO sample, 20<T<50, f=2.9 Hz Vexc=0.289 V

Unfortunately due to lots of noises above 40 K, Cp for BZPO sample could be obtained up to 40K. The suitable shape of Cp, shows that we are in good region of frequency for this sample. While for BCPO sample, wrong curvature again is a proof of wrong selected frequency. At the temperature around 32 I had to change PID, so discontinuity around 35 can be referred to this change.

5) In our fifth and last attempt, we selected frequency in the middle of our previous measurements. We increased frequency of BZPO a little to 3.4Hz, and for the second sample, BCPO, which is thicker we defined f=8.4Hz.figure (23), (24) and (25) are our plots for this conditions. We did our T-scan in the range of 5<T<41. To avoid of getting a lot of noise we selected a bigger excitation voltage 0.34 V.



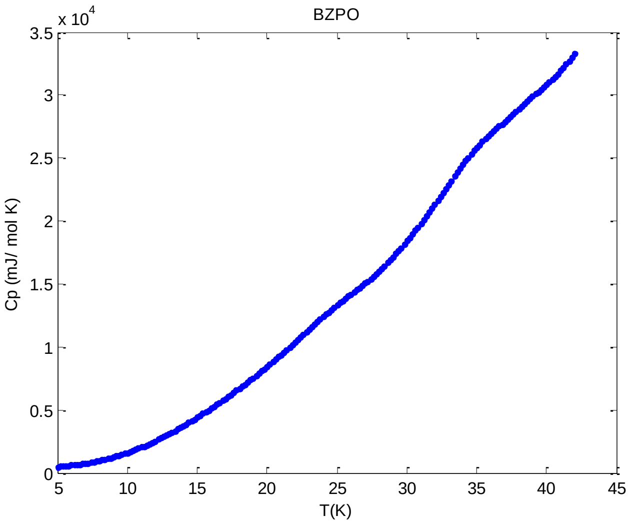


Figure (23), variation of a) vac, b) 1/vac and c) Cp with temperature for BZPO sample, 5<T<42, f=3.4 Hz, Vexc=0.34

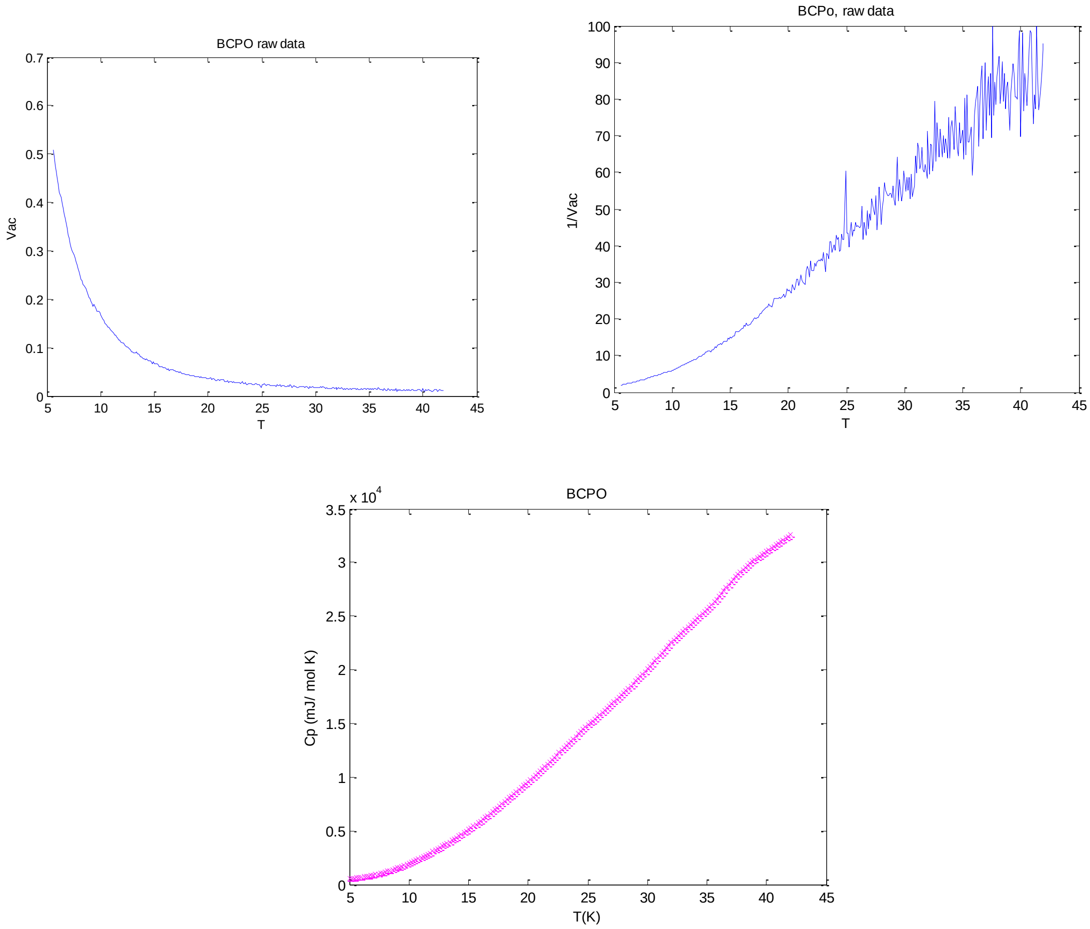


Figure (24), a) vac, b) 1/vac and c) Cp plots as a function of temperature for BCPO sample, 5<T<42, f=8.4 Hz, Vexc=0.34

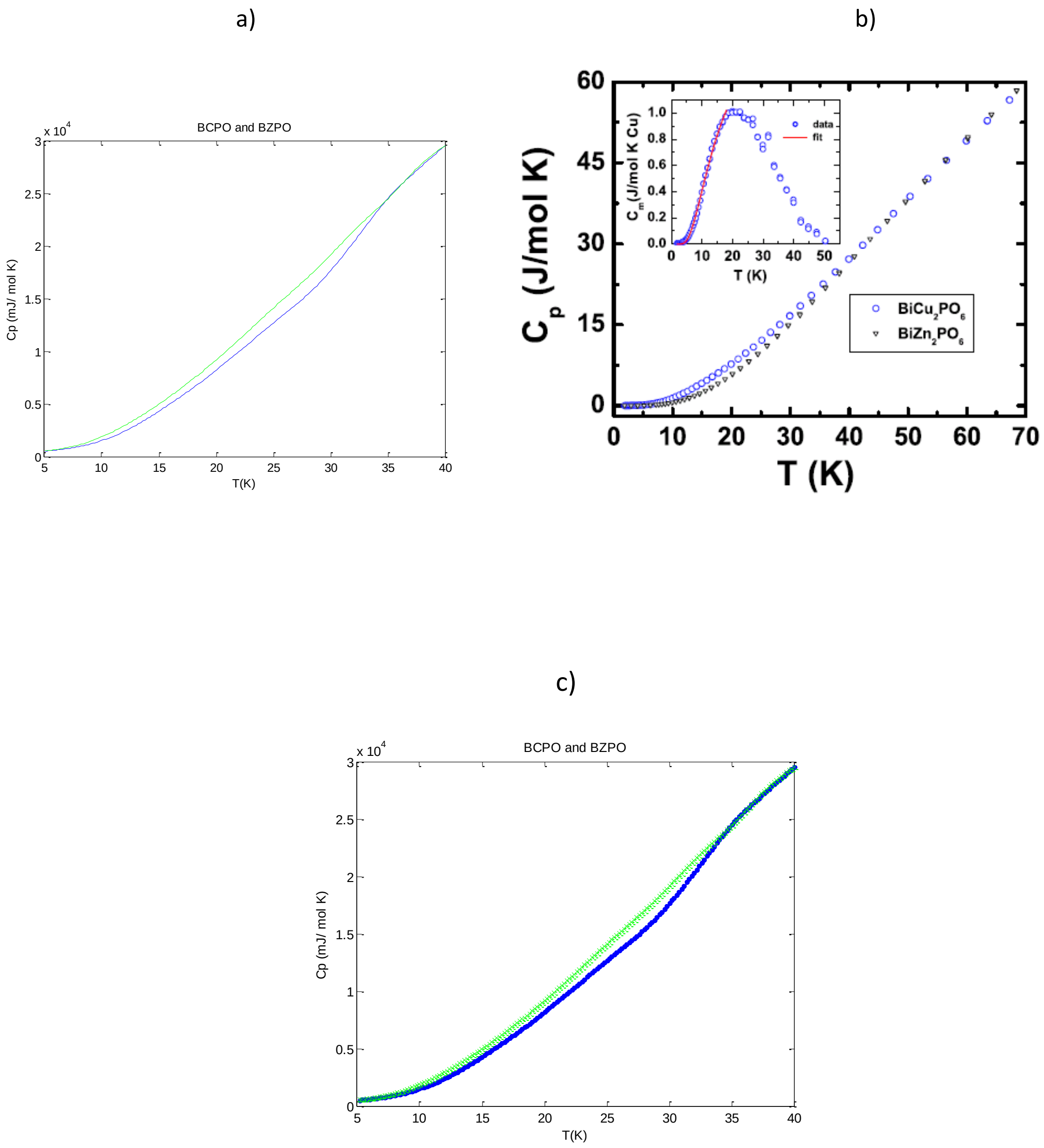


Figure (25), comparison of Cp of both samples, green curve BCPO, blue curve BZPO. 5<T<42, vexc=0.34 a and c measured data, b) literature reference.

13) Conclusion:

Doing a comparison between our measurement and literature, we see a good approximation for BCPO sample, while in BZPo there are some differences. In literature the main difference of Cp in both samples happens in temperature range [17, 27], while in our measurement this range is [27, 35]. This can be due to noise our effect of applied pressure.

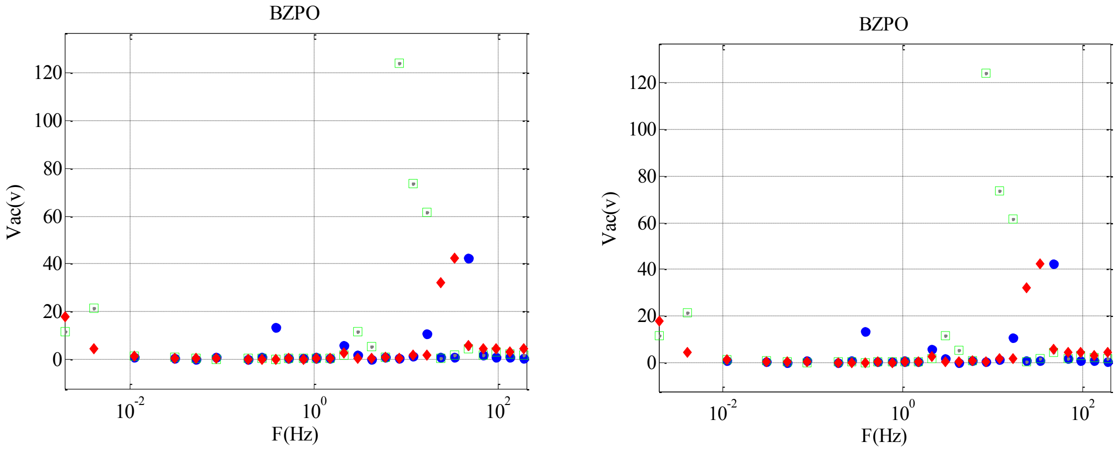
The reason of the difference between these two specific heats can be referred to a change in the magnetic part of the system. BCPO is a spin ladder system with a spin gap in its magnetic structure. By replacing completely Cu ion in the structure with non-magnet Zn ion, which has no magnetic momentum, we change its magnetic part. Specific heat has a phonon part as well, which is described by Debye model. Due to the same similarity between Zn and Cu, in radius and their place in Periodic Table, by replacing Cu with Zn, the phonon interactions stay intact, so the change in the specific heat can be explained as the change in the magnetic structure. On the other word, BZPO can be considered as phonon part of Cp in BCPO, that by subtracting its Cp from Cp of BCPO, we can derive magnetic specific heat of BCPO. One can find more information in reference [1].

14) Problems:

Unfortunately in this measurement, I couldn't get good result for temperature upper than 40 K, to show there is no difference between the specific heat of both sample above this temperature, but I got reasonable data for temperature below 40K.

The origin of such kind of problems may refer to experiment conditions or wires contact inside the samples. For example, whenever I had to take the VTI stick out to avoid Helium boil-off, I got a big noise in my measured data. PID parameter in lake shore, which is responsible of controlling bath temperature, sometimes didn't work for different temperature ranges, and I had to change it during the measurement which again led to a big noise in that temperature.

In the process of f-scan, sometime due to a wrong selected SEN, we entered the saturation regime and got not real data. Figure below show one of the measurement in which I got completely wrong data for f-scan of my samples. Although in some frequencies wrong measured data refers to not good set up in our system, but most of them are due to big noise that refers to experiment situations, (in this measurement I had to reduce AC gain to 20 db which is proof of existence the big noise in measurement situation). Figure (26) shows the result of this noisy measurement.



Figure(26), an example of the situation in which we got very large noise.

15) Outlook:

There are some solutions which can be used to avoid occurrence such kinds of problems. For instance, using silver paint instead of soldering or shielding the whole wires in the system can reduce the mechanical noises. Shielding whole wires is another practical way to decrease the effect of mechanical noise on experiment.

Writing the Python programming in a way which make the system aware of amplitude of measured voltage, and increase relevant parameter, such as SEN as needed, can solve the problems of saturated regimes.

Making system conscious of wrong selected PID, and make it capable to change PID of system automatic, can solve the problems regarding to thermalization and make the process of stabilizing temperature faster. For this solution, one way is to define a certain time for stabilizing of all temperatures, and if the process takes longer, make system capable to change PID to more favorable parameters.

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