University of Toronto
ADVANCED PHYSICS LABORATORY

# FE

# Ferroelectric materials and phase transitions

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## INTRODUCTION

One of the most successful applications of statistical physics is the description of phase transitions found in a wide variety of materials. Physical principles governing a superconducting phase transition are equally applicable to explaining the phase transition between nematic and smectic phases of liquid crystals. All (continuous, thermal) phase transitions can be classified into a number of universality classes determined by the system's physical dimensions and the symmetry of the order parameter.[1] It was also found that near various phase transitions, relevant physical quantities follow a power-law behavior with universal critical exponents. Determination of these critical exponents can help understand underlying model Hamiltonian of condensed matter systems. In this experiment, we will study ferroelectric phase transitions and measure critical exponents describing this transition.

In order to examine physical properties of solids, it is beneficial (often essential) to have a single crystal sample. A typical solid material encountered in your daily life is usually polycrystalline (almost all metals like copper wire, aluminum foil, etc. or ceramic toilet), which is a collection of numerous crystalline bits (think of grains of table salts) all tightly bound together. However, these crystalline bits are all randomly oriented, so physical properties that depend on the direction of the atomic arrangement are usually averaged. When you want to study ferroelectric order in which all dipoles are aligned in a particular direction, this averaging could make it difficult to determine physical properties. Many condensed matter physics experiments are carried out using single crystal samples when they are available (Often they are not!). Although it is generally very difficult to obtain a single crystal sample, some ferroelectric single crystals are very easy to grow. The students will grow their own single crystal samples to be used in this experiment.

## Ferromagnetic phase transition and mean field theory

A two-state paramagnetic system is a well-known model system often used in Thermal physics courses such as PHY252. This is a system described by a collection of spins (or magnetic dipole moments) following statistical principles. One can easily calculate energy, specific heat, and susceptibility as a function of temperature using partition function. You may recall that the susceptibility follows Curie's law. However, there is no magnetic order in this system. In other words, the total magnetization (order parameter) is zero in the absence of an external magnetic field. To make the system magnetically ordered, there has to be a non-zero interaction between the spins, but then the problem becomes somewhat complicated. One of the simplest ways to solve such a problem is called Weiss's mean field theory.[2]

According to mean field theory, the magnetic susceptibility is now described by so-called Curie-Weiss law:

$$\chi(T) = \frac{C}{T - \Theta} \qquad (1)$$

Where C is called Curie constant and $\Theta$ is the Curie-Weiss temperature. The order parameter (total magnetization M) is

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[1] The quantity that describes the degree of "order" in a system. For example, in a ferromagnet, the total magnetization is the order parameter. Order parameter decreases continuously as temperature rises, and becomes zero at the phase transition into disordered phase.

[2] See Chapter 8 of Schroeder's Thermal Physics textbook

$$M(T) = M(0)(1 - T/T_c)^{1/2} \qquad\qquad (2)$$

Where $T_c$ is the phase transition temperature, and M(0) is the value of order parameter at T=0. These results are shown schematically in Figure 1.
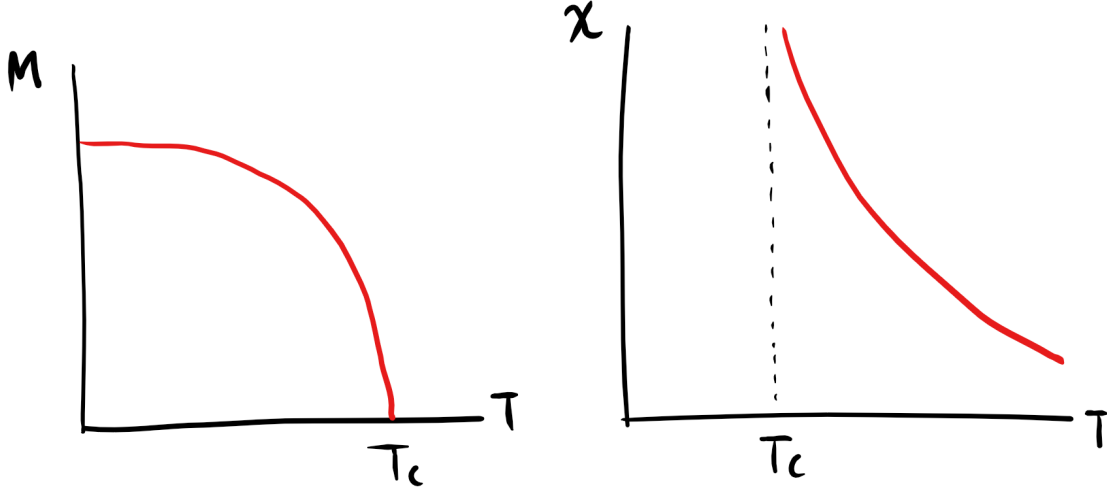


Figure 1 Magnetization M(T) and susceptibility $\chi(T)$

As you can see from Eq. (2), the order parameter decreases continuously with increasing temperature and vanishes at $T = T_c$. The abruptness of the disappearance is described by the exponent ½ in Eq. (2). Mean field theory predicts square root behavior, but advanced theory suggests that this exponent (often labeled beta) is closer to 1/3 in real three dimensional materials, and often smaller in two dimensions.

Although the order disappears at $T_c$, physics for $T > T_c$ is no less interesting. Thinking about approaching the continuous phase transition from high temperature side is useful for this. As temperature is lowered and approaches Tc, the spins do feel the tendency to order, which is called fluctuations. That is, although they are not ordered statically over a long range, they may "look like" ordered for short duration over short distance. The fluctuation grows with decreasing temperature, and eventually diverges, when the system orders. The experimental measure of this fluctuation is susceptibility in Eq. (1). Experimental definition of magnetic susceptibility is usually given as

$$\chi = \left.\frac{\Delta M}{\Delta B}\right|_{\Delta B \to 0}$$

That is, the amount of magnetization induced when an infinitesimally small magnetic field is applied. Therefore, when the system has a strong tendency (fluctuation) to order, the susceptibility will be large. Mean field theory predicts that the susceptibility diverges with exponent 1. Equation (1) above can be rewritten as $\chi \propto (T - T_c)^{-1}$.

## Ferromagnetic domains and hysteresis

Now, consider the magnetically ordered phase $T < T_c$. You can think about the 2-state magnetic problem from thermal physics. When the system orders at $T_c$, how does it choose which direction to point to? Remember that all spins pointing up is equivalent to the order in which all

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spins are pointing down. The answer is that the choice is random. Often in nature there exists small things that break the symmetry. For example, some small magnetic field due to the earth or electronic devices in your house might do the job. But in general, this happens randomly, and in a large sample with billions and billions of spins, some part of the sample will point up, while the other part will point down, and these "regions" of the sample with different magnetization direction are called magnetic "domains". Due to these domains, when you measure M as a function of applied field $B$, they follow a characteristic line called hysteresis loop. An example is shown in Fig. 2 below.
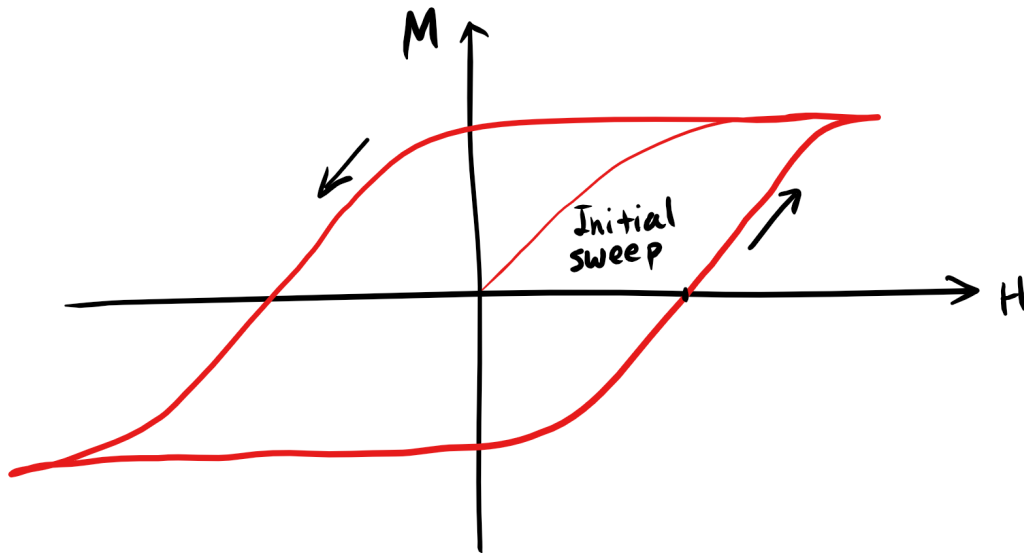


Figure 2. Hysteresis loop (M vs H curve) of a ferromagnet

## Ferroelectricity

So far we have been discussing the ferromagnetic-paramagnetic phase transition, which occurs in a magnetic system composed of interacting spins. Now, remembering that the spin is just a magnetic dipole moment, let's replace "magnetic" with "electric" in above discussions. As you can guess, physics of ferroelectric-paraelectric transition is analogous to the ferromagnetic-paramagnetic transition, and the equations describing dielectric susceptibility and ferroelectric polarization are given by exactly the same equations (1) and (2) according to mean field theory.

Now, one might ask, what do you mean by "electric dipole"? What about the electric charge? That's a very good question. An electric dipole is not a fundamental unit like electron spin, but a composite object made up with positive and negative charges. So microscopic description at the level of atoms and electrons is more complicated. What's really happening in real ferroelectric materials is shown in Fig. 3 for the example of $BaTiO_3$, In the paraelectric (disordered) phase, $Ti^{4+}$ ions are located at the center of a cubic unit cell (unit cell is like a molecular Lego block, and by stacking them you can build up a crystal), and all ionic charges are balanced. In ferroelectric phase, however, the $Ti^{4+}$ ion moves along the +z-direction, so that the top half of the unit cell has more positive charge than the bottom half of the unit cell. That is the unit cell now has an electric dipole moment.

*Question: Assuming that the Ti$^{4+}$ ion moves by 0.1 angstrom, what is the value of the dipole moment?*

*Question: Although the analogy between the spins in magnets and the electric dipoles in dielectric materials is very good, there is a fundamental difference between them, that is crucial for a deeper understanding of ferroelectric transition.  Can you think of differences?*
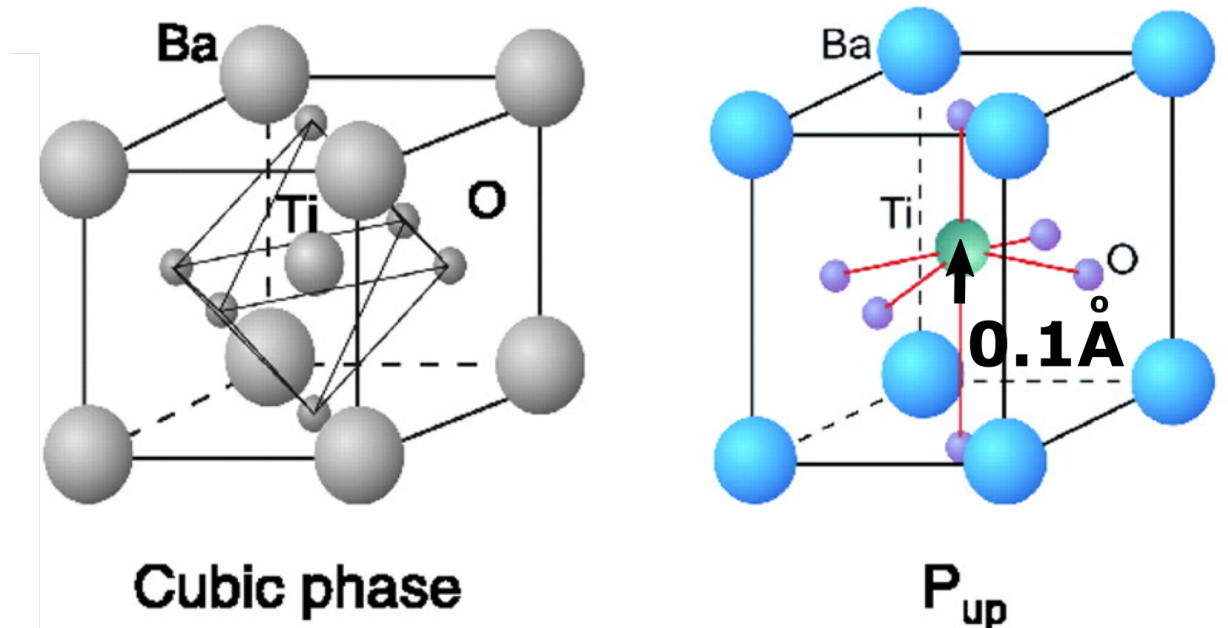


Figure 3. Paraelectric (disordered) phase and ferroelectric phase with polarization pointing up in BaTiO$_3$  The Ti4+ ion is pushed up by 0.1 Å in the ferroelectric phase. (from Ahn et al. Science 303, 488 (2004)).

## Dielectric constant measurement

The physical quantity we are interested in this experiment is called dielectric constant, which is really a misnomer since it is not really a constant.  This quantity essentially tells you how your material responds when an external electric field is applied, which depends on the frequency of electric field and temperature of the material.  If you recall our definition of magnetic susceptibility, it is tempting to call this quantity (di)electric susceptibility.  But actual electric susceptibility, $\chi_e$, is related to dielectric constant by the relation: $\epsilon/\epsilon_0 = 1 + \chi_e$, where the quantity $\epsilon_0 = 8.85 \times 10^{-12}$ (C$^2$N$^{-1}$m$^{-2}$) is the permittivity of vacuum.  That is, the electric susceptibility becomes zero in vacuum.  Since $\epsilon \gg \epsilon_0$ in most ferroelectric materials, measuring dielectric constant is equivalent to measuring electric susceptibility.  Now, you probably first heard about dielectric constant when you studied a unit on a capacitor.  Recall that the capacitance of a parallel plate capacitor with area A and separation d is given by

$$C_0 = \frac{\epsilon_0 A}{d}$$

When the space between the two plates is filled with a dielectric constant $\epsilon$, the capacitance is $C = \epsilon A/d$. Therefore, the ratio $C/C_0$ is a good measure of dielectric constant with respect to the vacuum permittivity.

The most straightforward method to measure the dielectric constant is to measure the capacitance with high accuracy. The sample is cut into a plate-like shape and electrodes (metallic surfaces) are placed on top and bottom of the sample to make a parallel plate capacitor. Then by just measuring the capacitance as a function of temperature one can obtain the dielectric susceptibility as a function of temperature. There are a number of methods to measure the capacitance. Some multimeters are usually equipped with an option to measure capacitance down to 1pF, which is sufficient for the purpose of our measurement. Higher accuracy can be obtained by using a capacitance bridge. In this experiment, you will use the M6013 Capacitance meter, which can measure down to 0.01 pF (nominally).

## Ferroelectric materials

There are many different types of ferroelectric materials, and they are subjects of intense research efforts. There are many applications for ferroelectric materials, including FRAM, an example of non-volatile memory chips. Many of ferroelectric materials also exhibit piezoelectricity. Piezoelectric materials either shrink or expand when an electric field is applied. Since electric dipoles are aligned in ferroelectric phase, atoms in ferroelectric materials are subject to an intense local electric field, resulting in atomic structure change, which in turn changes the shape of the crystal. Piezoelectric materials such as PZT (based on $PbTiO_3$ and $PbZrO_3$) is one of the most important materials for technological applications. Since piezoelectric materials allow mechanical control without using complicated machinery, it is widely used in small scale mechanical devices. One of the best-known examples is its use as a tip in scanning tunneling microscope (STM). Nowadays, piezoelectric devices have replaced traditional electric motors in many applications. A simple example of ferroelectric materials is $BaTiO_3$ (BTO) and other perovskite based structure, which is the examples used to describe the ferroelectric phenomenon in Fig. 3.

In this experiment, you will focus on Rochelle salt. Potassium sodium tartrate tetrahydrate ($KNaC_4H_4O_6 \, 4H_2O$), usually called Rochelle salt, is a very useful material used in medicine as well as early phonographs (See van Klooster [5] or Wikipedia for details). This was also the first piezoelectric material discovered in early 19th century. Since this is one of the easiest crystal to grow, it is often used in crystal growth kits for school children.

Rochelle salt normally has a rhombic crystal structure, but between -18°C and 24°C it becomes monoclinic. The rhombic phase is paraelectric, while the monoclinic phase is ferroelectric. The two ferroelectric phase transitions can be easily detected by measuring dielectric constants across the two transition temperatures. Although Rochelle salt is easy to prepare and has relatively convenient ferroelectric transition temperature, it is not widely used in modern applications due to the fragility of the crystal. As you will find out the crystal is quite brittle, so you need to be careful in handling the crystal. It is also water soluble (the crystal is grown in water solution), which means that if the crystal is in contact with water, it will disappear (or in very humid condition). Also, the crystal disintegrates at relatively low temperature of about 50C. So you cannot use any heat treatment. You have to be careful when you measure the dielectric susceptibility of this crystal to make sure you don't lose your sample!

## EXPERIMENT

The experiment's objectives are:

1. Grow a large enough Rochelle salt crystal to measure its ferroelectric properties. Your first goal is to obtain a sizable crystal, but you will also need to shape the crystal for parallel plate capacitor geometry.
2. Measure temperature dependence of dielectric susceptibility and investigate Curie-Weiss behavior by fitting the data to Equation (1).
3. Study the hysteresis loop of Rochelle salt as a function of temperature. You can obtain electric polarization (order parameter) as a function of temperature, and fit your result to Equation (2).

## Part I. Growing a single crystal sample of Rochelle salt (Charles Zheng)

Obtaining a single crystal sample with a high degree of crystallinity and low concentration of defects is one of the most important (and difficult) steps in condensed matter physics research, and there are many books and research papers devoted to this topic. There is even a journal called Journal of Crystal Growth. Potassium sodium tartrate tetrahydrate ($KNaC_4H_4O_6 \cdot 4H_2O$), also known as Rochelle Salt, is a ferroelectric crystal that can be easily made using commonly available household ingredients. The principle is quite simple. You first create a supersaturated solution of Rochelle salt. Then slow evaporation of water will cause the sample to precipitate and begin forming small crystals. If, somehow, you can limit the precipitation point to one, all

Rochelle salt will form one single crystal. This is usually very difficult, but by trial and error, you can probably grow reasonably large (1~2 cm) single crystals. The ingredients you will need are

- Cream of Tartar: Also known as potassium bitartrate ($KHC_4H_4O_6$), is a baking ingredient.

- Sodium carbonate (Na2CO3) is a laundry detergent booster usually called washing soda. However, this is not easy to find. It is much easier to find sodium bicarbonate (NaHCO3), which is baking soda. You can convert this into sodium carbonate easily. If you heat baking soda at 200C for about an hour, the baking soda will decompose into washing soda, giving off CO2 and water in the process via 2NaHCO3 ➔ Na2CO3 + CO2 + H2O. Let the washing soda cool to room temperature before using.

Rochelle salt can be formed by mixing the two ingredients above in water. The reaction is as follows:

$$2KHC_4H_4O_6 + Na_2CO_3 + 8H_2O ➔ 2KNaC_4H_4O_6 \cdot 4H_2O + H_2O + CO_2 \text{ (gas)}$$

Before starting the crystal growth, you need to determine how much ingredients are needed based on the above stoichiometry equation. For example, if we want to produce 0.2 mole (about 56 g) of Rochelle salt, we need to use 0.2 mole (about 38g) of cream of tartar and 0.1 mole (about 10g) of sodium carbonate.

The goal of the crystal growth is making a supersaturated solution of Rochelle salt at room temperature, which means that the amount of Rochelle salt in the solution is more than the water can handle. This excess salt will precipitate and form crystals. As water evaporates slowly more salt will precipitate. The easiest way to make supersaturated solution is to heat the solution slightly above the room temperature. Since solubility of the salt is higher at high temperature, more salt will dissolve, and when the solution is cooled down to room temperature, it will be supersaturated.

Step by step instructions:
1) Clean the glass containers you will use for the growth using soap and water and dry completely.
2) Measure distilled water necessary (about 50 ml) and put it in a beaker.
3) Pour in your cream of tartar and mix it until all of it dissolves. Your solution should be milky at this point.
4) Now slowly add in the sodium carbonate. You can add about a teaspoon at a time initially. When it is added, stir the solution. You should see lots of bubbling and fizzing. This is the $CO_2$ being produced. Keep stirring until the fizzing stops, indicating that the sodium carbonate has been used up. Then continue to add more, slowly. Here are some tips and cautions:
   a. DO NOT add more sodium carbonate until the fizzing has stopped.
   b. This step requires LOTS of patience. It is very common for the solution to fizz for more than 10 minutes after each addition of sodium carbonate. You need to keep stirring at all times.
   c. Keep the temperature of solution at constant value slightly above the room temperature. (50-60C)

d. As you add more sodium carbonate, you may notice that it takes longer for the fizzing to start. This is an indication that the cream of tartar is almost used up. At this point, you need to be especially careful. Add only pinches of sodium carbonate at a time.

e. As more sodium carbonate is added and reacted, the solution should slowly turn less milky. When all of the cream of tartar has reacted, the solution should be clear (perhaps with a slight yellow tone).

f. This is the ideal scenario, and it is when you should stop adding more sodium carbonate. However, if your solution is still milky but you notice that the solution will not fizz even 10 minutes after adding sodium carbonate, you can stop.

5) Filter your solution into a clean container (wide cylinder to increase surface area) using a clean filter paper and a clean funnel. After filtering, your solution should be relatively clear. (If you don't know how to use a filter, see http://faculty.sites.uci.edu/chem1l/files/2013/11/RDGfiltration.pdf )

6) Find an undisturbed location that is relatively dust free and not subject to large temperature fluctuations. Leave your solution there with the top covered to prevent from dirt to fall in. (Note: It is important that the location is not subject to large temperature fluctuations. The solubility of rochelle salt in water has a considerable temperature dependence. If the temperature of the environment is constantly changing, your solution will oscillate between being supersaturated and undersaturated. Any crystals that form when the solution is supersaturated will dissolve again when the solution becomes undersaturated.

7) As the solution cools down and water evaporates, the solution will eventually become supersaturated and the rochelle salt will be forced out of the solution to form crystals.

8) Be patient at this stage. You will need a couple of days to see crystal growths. Leaving the container over the weekend without being disturbed is a good idea.
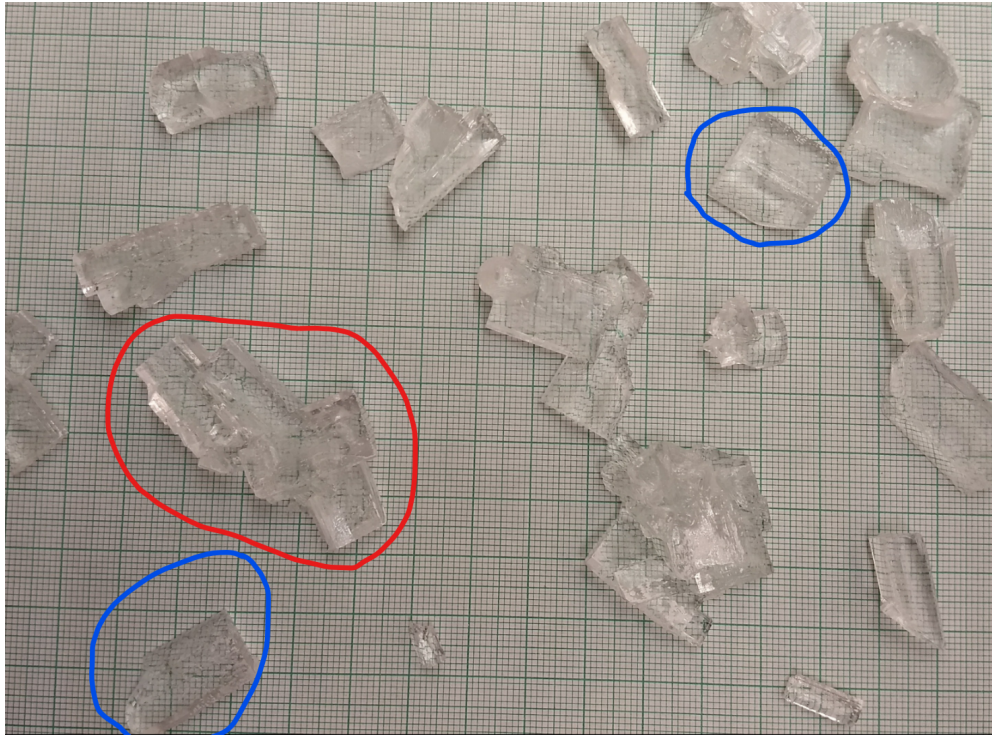
Figure 4. Rochelle salt crystals. This is what you might get at the end of step 8. Some crystals are single grain (blue circles), and some other pieces are made up of intergrowth of different grains of crystals (red circle). You will use single-grain crystals.

## Preparing Rochelle salt crystal for dielectric measurement

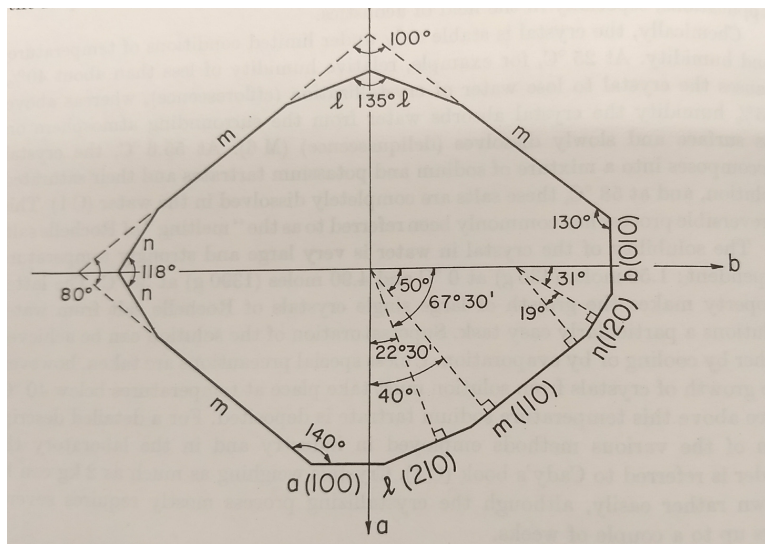The Rochelle salt crystal usually exhibits so-called habits as shown in figure 5.



Figure 5. Morphology of Rochelle salt. The drawing represents the cross-section perpendicular to [001] of an ideal crystal (schematic). The angles are approximate. (From Jona and Shirane, *Ferroelectric Crystals*)

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Rochelle salt exhibits the largest dielectric response when an electric field is applied along the [100] direction. Therefore, you want to make a thin plate with plate normal along the direction [100]. The simplest way to shape a Rochelle salt crystal is by grinding the sample sand paper with water as a lubricant. Since Rochelle salt is water soluble, this can get rid of the sample quite quickly, so you should pay careful attention. Otherwise, your sample will be gone! Always have a paper towel or kimwipe ready nearby so that you can stop water from dissolving the sample once you reached the desired thickness. Also, you should try your best to make two parallel faces to ensure parallel plate geometry.

Use silver paint (Pelco 16062) to make conducting plates and also to attach wires. It takes time for the silver paint to dry (several hours, 24 hours recommended). Do not try to dry silver paint by heating it – You Will Destroy the Sample! Therefore, it is a good idea to secure the electrical wires using masking tape on a microscope glass (See figure 6). Note that the wires usually have an insulating coating, so you need to sand this coating layer off before making any electrical connection.
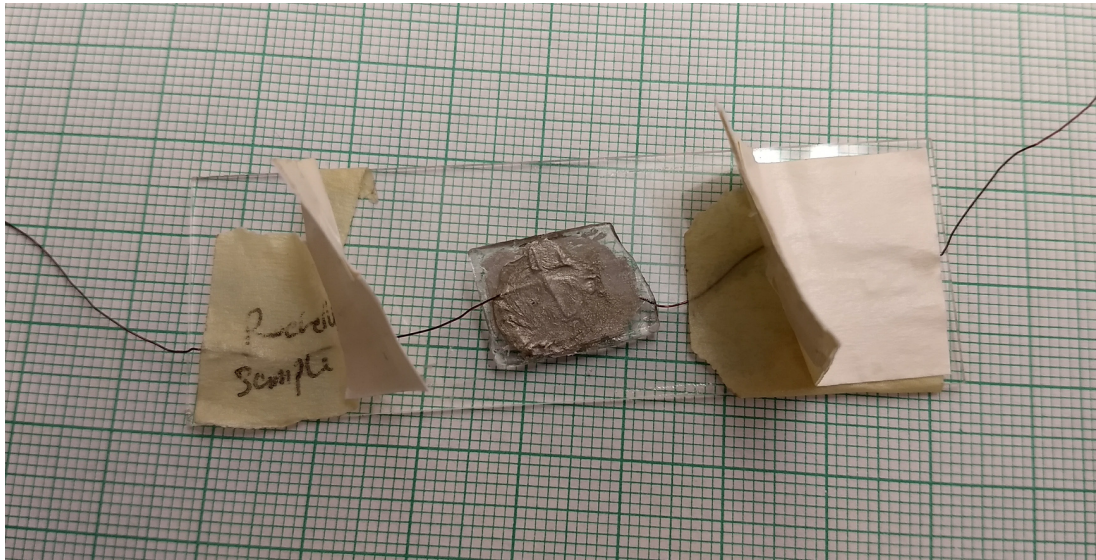


Figure 6. Example of Rochelle salt crystal with silver paint as a conducting plate. The wire is attached using silver paint (Pelco 16062) and cured at room temperature for 24 hours.


**Question:** What will be the approximate capacitance of the parallel plate capacitor you built using the Rochelle salt crystal? You have to measure the dimensions of the sample.

## Measurements

### A. Dielectric constant as a function of temperature

The temperature control will be provided by thermoelectric cold plate, which can reach below 0 C. To keep the temperature stable, it is advised to cover your sample using a petri dish as shown in Figure 7. The temperature should be monitored using the thermocouple. This will of course only allow you to access room temperature and below. To go to higher temperature, you will need to use heat gun (hot air blower) while still staying on top of the cold plate. A capacitance

meter is provided that can be used to measure the capacitance. You may want to wait a while after setting the temperature until temperature reaches equilibrium.

Caution:

- Be careful not to heat the sample above 50C. Otherwise the sample will disintegrate.
- The top of the cold plate is a conductor. You should use a microscope glass to *electrically* insulate your sample from touching the cold plate.



Figure 7. Thermoelectric cold plate and the petri dish used as a cover. The cover is used to keep the air inside the petri dish more or less stable.

For your analysis, the best method to illustrate power law behaviour is a logarithmic plot. You will see that to have a large range in the logarithmic plot, it is most useful to obtain the data as close to the transition temperature as possible.

## B. Ferroelectric hysteresis loop and polarization

Hysteresis loops of P vs E can be generated on the oscilloscope by using a Sawyer-Tower circuit shown in Fig. 8. The voltage across the ferroelectric sample capacitor is applied to the horizontal plates of the oscilloscope (X). The reference capacitor is in series with the sample. The voltage across the reference capacitor is proportional to the polarization of the sample and applied to the Y input of the oscilloscope. You can start your measurement with a 2nF reference capacitor.
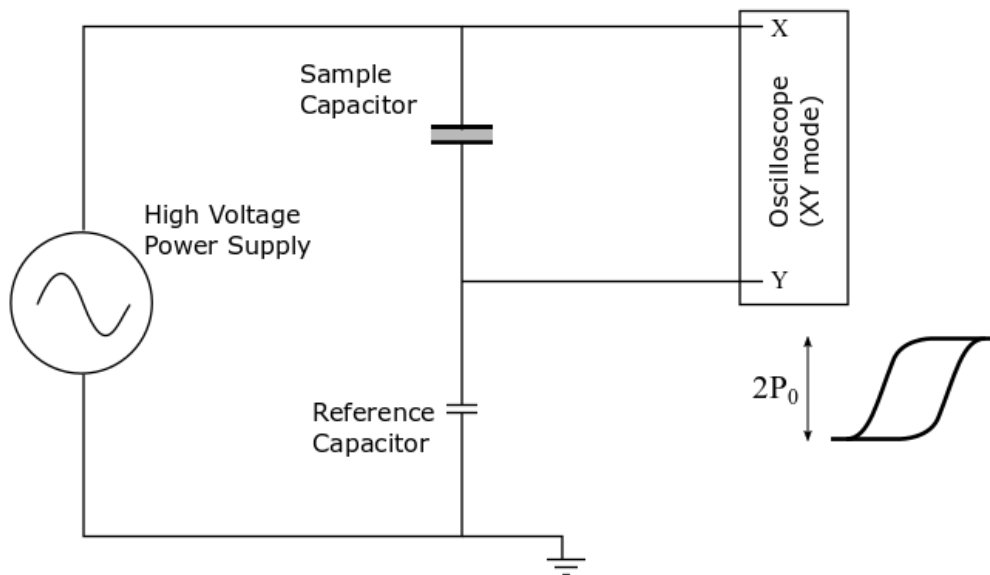
Figure 8. Modified Sawyer-Tower circuit for measuring P vs E hysteresis loop.

Since the spontaneous polarization is the order parameter of ferroelectric order, you may want to measure the polarization as a function of temperature in order to obtain the order parameter plot as shown in Fig. 1. The spontaneous polarization can be determined from the saturated polarization value from the hysteresis curve ($P_0$ in Fig. 8). The order parameter should follow a power law temperature dependence (Equation 2).

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