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Ferroelectricity

[redacted]

Physics 122

March 14, 2005

Abstract

A wafer of ferroelectric material triglycine sulfate (TGS) is used to demonstrate ferroelectric properties such as specific behavior of the dielectric constant, spontaneous polarization and hysteresis loops.

The Curie temperature, at which a phase transition occurs, is central to much of the theory behind ferroelectricity. The Curie temperature was obtained using three different methods and the values obtained were 48.2, 48.5, and 48.0 degrees Celsius.

The dielectric constant and capacitance of the ferroelectric sample were observed to reach maximum values at the Curie temperature as theoretically predicted.

The relationship between spontaneous polarization and temperature was found to confirm the theoretical prediction, especially below 36 degrees Celsius.

The hysteresis loops produced from plots of displacement versus electric field also confirmed theoretical understanding of the behavior or ferroelectric materials.

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Introduction

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Motivation and Goals:

Several characteristics of ferroelectric materials will be demonstrated using the ferroelectric material triglycine sulfate (TGS). Observing various changes in the properties of the material under different conditions facilitates greater understanding of ferroelectric materials and of ferroelectricity.

The behavior of the dielectric constant above and below the Curie temperature will be observed using a multimeter to measure the sample's capacitance; the observed behavior can then be compared to the predicted behavior. The dielectric constant is a maximum at the Curie temperature, so by measuring the temperature at which the TGS sample has the highest dielectric constant, the experimental value of the Curie temperature can be obtained.

The temperature dependence of the spontaneous polarization of the TGS sample will be obtained and compared to the theoretical relationship between spontaneous polarization and temperature.

Measurements of the electric field and the displacement vector in the sample will be used to produce hysteresis loops at various temperatures. The slopes of the curves in the loops on the plot of D vs. E correspond to values of the dielectric constant. The temperature corresponding to the hysteresis loop displaying the greatest slope can be found and thus the Curie temperature can be obtained experimentally by this method.

Theoretical Background:

The properties of ferroelectric materials such as triglycine sulfate (TGS) change with temperature, especially near the Curie temperature.

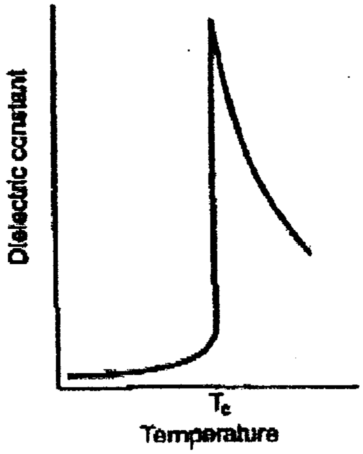
The dielectric constant of TGS theoretically changes with temperature according to the Curie-Weiss law:

$\varepsilon = 1 + C / (T - T_c)$, where C is the Curie constant and T_c is the Curie temperature

This relation works for temperatures greater than the Curie temperature, which must be positive. Near the transition (Curie) temperature, the dielectric constant reaches a maximum. At temperatures below the Curie temperature,

$$\varepsilon = 1 + C / 2(T_c - T)$$

The relationship between dielectric constant and temperature is shown below:



(Image from Reference #1)

The dielectric constant is proportional to the TGS sample's capacitance, which can be measured using a multimeter. Temperature of the TGS sample can be monitored using a thermocouple (copper-constantan) which is glued to the TGS and connected to a regulator, which displays a set value as well as the present value of the temperature. By recording the capacitance measurements corresponding to different temperatures of the sample both above and below the expected Curie temperature, the predicted relationship should be apparent. The Curie temperature can be experimentally determined by finding the temperature corresponding to the maximum capacitance value obtained from the multimeter.

A phase transition occurs at the Curie temperature; above this temperature the elementary dipoles of the various unit cells in the crystal are oriented randomly and below the Curie temperature elementary dipoles interact with each other, giving rise to an internal electric field which lines up the dipoles along a favorable orientation within the crystal.

When the ferroelectric sample temperature is below the Curie temperature, the material becomes spontaneously electrically polarized, aligning the electric dipoles in the material without the influence of an external electric field. The spontaneous polarization increases gradually as the temperature decreases farther below the Curie temperature.

Spontaneous polarization of the sample can be measured using an electrometer, which measures the charge on the conducting electrodes on the surface of the sample. There are free charges on the electrodes bonded to the sides of the sample, but there are also charges on the faces of the sample due to its polarization. The polarization charges can be observed when the sample is completely polarized, i.e. the crystal is in a single-domain state. The sample is heated above the Curie temperature, then a DC voltage is applied to the sample capacitor faces. The polarization is aligned by this voltage as the sample is then cooled through the transition temperature. Once the sample is below the transition temperature, the polarizing voltage is removed but the spontaneous polarization in the sample is still present because the sample is in a ferroelectric state. At this point there is a bound surface charge with density equal to the magnitude of the sample's polarization on one side of the sample and an equal and opposite bound charge on the other side. Each of these quantities of bound charges is also associated with an equal amount of free charge. Heating the sample from this ferroelectric state to the normal state above the transition temperature causes the spontaneous polarization to diminish along with the bound charge. Thus, the free charges are in excess and can flow from one side of the sample to the other as long as the two sides of the sample are connected (short circuited). An electrometer connected in series with the sample measures the changes in the free charge by measuring the amount of charge that flows across the sample.

The charge theoretically increases along with the temperature until the transition temperature is reached. At the transition temperature the polarization is theoretically zero so the charge measured at this temperature gives the initial free charge from the conducting electrodes. The charge measured at each different temperature can then be subtracted from this value to obtain the charge due to polarization.

The expected behavior of the spontaneous polarization, P_s, can be described by the following equation:

$$P_s^2 = (T_c - T) / (4\pi gC)$$, where g is generally a function of temperature and C is the Curie constant

So, P_s is theoretically proportional to $(T_c - T)^\wedge(1/2)$.
This equation for the spontaneous polarization is derived from mean field theory of the phase transition:

There is a local electric field, E_{loc}, described by the sum of the applied electric field, E, and the electric field due to polarization charges on the boundaries of the material. The field due to polarization charges is proportional to the polarization vector, P, so E_{loc} is described by:

$$E_{loc} = E + fP$$, where f is a constant of proportionality

It can be noted here that P is defined by the equation for displacement, D:

$$D = E + 4\pi P$$

This relates the dielectric constant and electric susceptibility, which are, respectively:

$$\varepsilon = D / E \text{ and } \chi = P / E$$

Thus,

$$\varepsilon = 1 + 4\pi\chi$$

Since the local electric field is a function of the polarization, it can be expanded in a power series as follows:

$E_{loc} = g_1P + g_2P^3 + g_3P^5 + \ldots$, where the g coefficients are generally functions of the temperature and even powers are omitted because they would not result in the proper symmetry to describe how E_{loc} reverses the applied electric field

Thus,

$E = E_{loc} - fP \approx (g_1 - f)P$, where the higher order terms have been neglected since P is very small above the Curie temperature

Assuming that g_1 and f are proportional to temperature and that $(1/4\pi C)$ is a valid constant of proportionality,

$$g_1 = T / (4\pi C) \text{ and } f = T_c / (4\pi C)$$

Substituting these values into the equation for E gives the Curie-Weiss law and the equation for the dielectric constant given earlier: $\varepsilon = 1 + C / (T - T_c)$, for $T > T_c$.

Below the Curie temperature, the spontaneous polarization appears with no applied electric field:

$$E = (g_1 - f)P_s + + g_2P_s^3 + g_3P_s^5 + \ldots = 0$$

Typically, near the transition temperature the fifth-order term and higher can be neglected, giving the equation for the spontaneous polarization, P_s:

$$P_s^2 = (f - g_1) / g_2 = (T_c - T) / (4\pi g_2 C)$$

Application of an external electric field, ΔE, here would change the polarization by ΔP:

$$\Delta E = (g_1 - f)(P_s + \Delta P) + g_2(P_s + \Delta P)^3 + \ldots$$

By dropping terms in ΔP^2:

$$\Delta E = (g_1 - f)\Delta P + 3g_2P_s^2\Delta P + \ldots$$

Use the equation for the spontaneous polarization, P_s, to obtain:

$$\Delta E = 2(f - g_1)\Delta P$$

Thus, for this equation, the electric susceptibility is defined by $\chi = \Delta P / \Delta E$, so the increment is used rather than the full polarization. This is desirable for having the susceptibility measure the effect of the applied field, ΔE, on the sample. This equation can also be used to obtain the equation given earlier for the dielectric constant for temperatures below the Curie temperature:

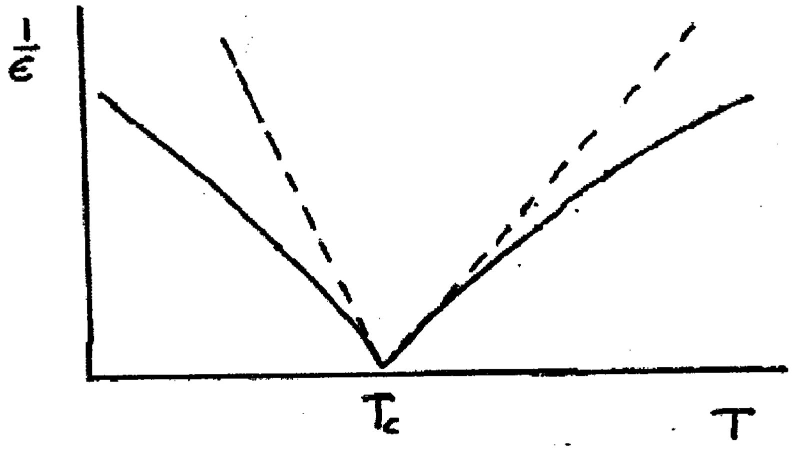
$$\varepsilon = 1 + C / 2(T_c - T)$$

The equations for the dielectric constant below and above the Curie temperature can be expanded about $T = T_c$ to obtain:

$$(1/\varepsilon) = (1/C)(T - T_c) \quad \text{for } T > T_c$$

$$(1/\varepsilon) = (2/C)(T_c - T) \quad \text{for } T < T_c$$

These equations sum up the behavior of the dielectric constant and demonstrate the sudden change that occurs at the transition temperature:



(Image from Reference #1)

In ferroelectric crystals, the direction of the spontaneous dipole moment can be altered by an electric field. A plot of the displacement vector in the sample versus the electric field, E, is interesting to observe. Since the dielectric constant, ε, is proportional to D / E, the slope of this curve represents the dielectric constant of the ferroelectric sample. The curve with the steepest slope corresponds to the maximum value of the dielectric constant and therefore would occur at the Curie temperature.

The curves of displacement versus electric field form hysteresis loops. This is because as the applied electric field increases, the polarization increases, increasing the displacement, D, in the sample:

$$D = \varepsilon_o E + P$$

Eventually the sample is completely polarized with all of the electric dipoles aligned and a further increase in the electric field has no effect on the polarization. If the electric field is then reduced, the dipoles may gradually return to randomly oriented domains, reducing the polarization, P, and thus reducing the displacement, D. If, however, the crystal is at a temperature such that it is in a ferroelectric state, polarization will be present due to the temperature even as the polarizing electric field is reduced. In this case, while the electric field still has relatively high values, this together with the temperature-induced polarization will cause a high value for the displacement, D, which will eventually decrease as the electric field gets very small.

Experimental Setup and Procedure

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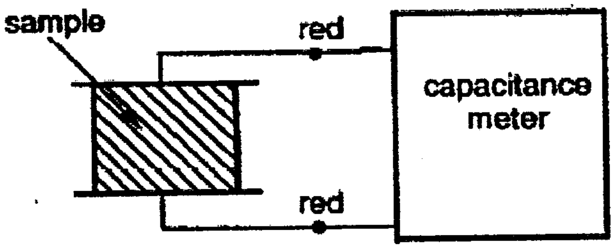
Experimental Setup:

The ferroelectric sample is a wafer of triglycine sulfate (TGS) with opposite sides painted with conducting paint to form a capacitor. The area of the wafer is about 1 cm^2 and its thickness is about 1mm.

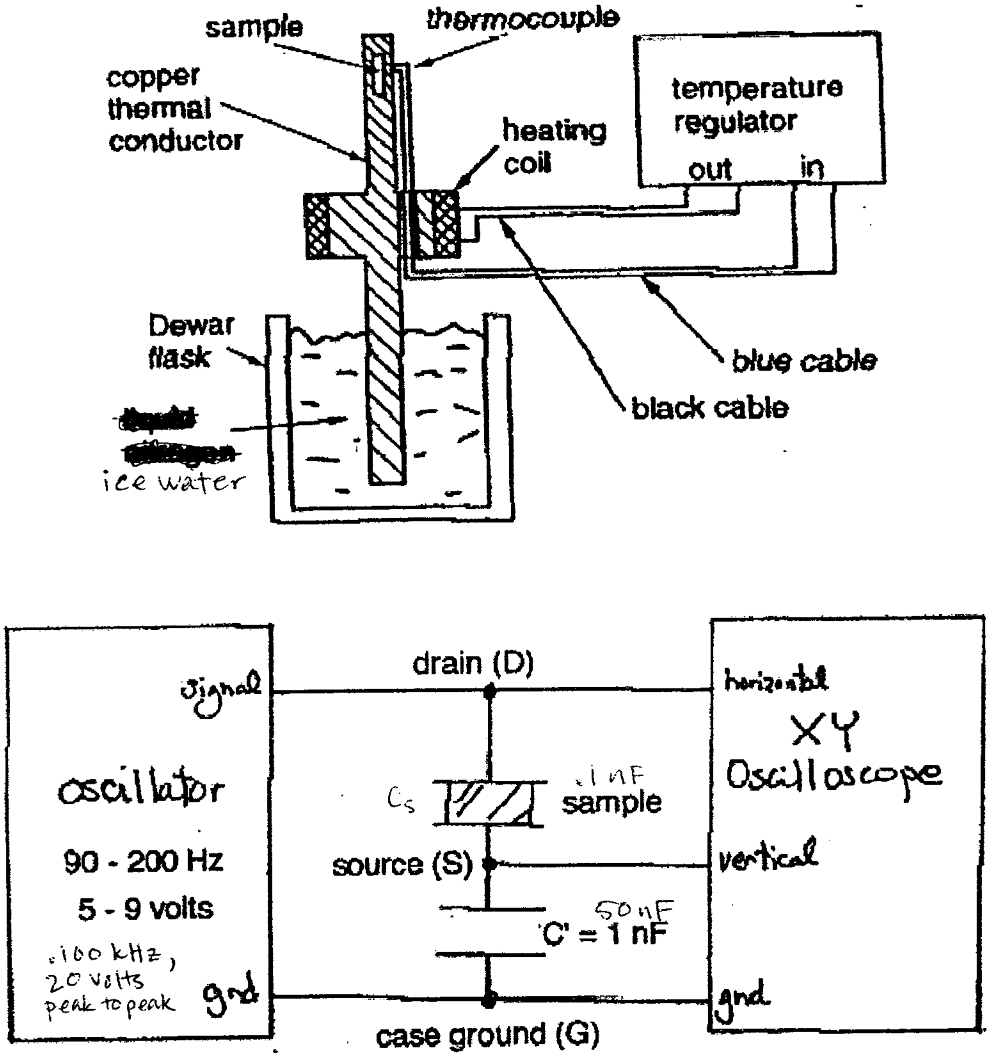
The capacitance of the sample (which is proportional to the dielectric constant) was measured using a BK Precision 810A multimeter. The multimeter was set to measure up to 2 nF and the error was +/- .001 nF.



(Image from Reference #1)

Temperature was measured using a thermocouple (copper-constantan) that is glued to the TGS sample. The thermocouple is also connected to an Omega CN76000 regulator, which displays a set temperature and the present value of the temperature of the sample. The set value can be changed using buttons on the display and the regulator works to make the temperature of the sample approach the set temperature.

Ice water and a heating coil were used to control the temperature of the sample. Ice water is sufficient for cooling the sample because the experiment is conducted between about 0 and 60 degrees Celsius. The heater was turned on or off using a variac dial to control the voltage across the coil. The sample was suspended over (from the lid of) a dewar flask which was filled with the ice water up to the fill line. Connected to the sample was a copper conducting rod that made contact with both the ice water inside the dewar flask and with the heating coil on the lid of the flask. The flask setup is pictured here:



Sample (in flask setup) connected to function generator (oscillator), oscilloscope and reference capacitor, C'. Locations of D,S, and G are shown. (Images from Reference #1)

Procedure:

Temperature Dependence of the Dielectric Constant:

The dewar flask was filled with ice water six hours before taking measurements to allow time for the conducting rod and sample to reach the ice water's temperature. The sample was cooled to 8.3 degrees Celsius, which was the starting temperature for the measurements.

The multimeter was set to read capacitance and a reading was taken from the meter with no sample present to determine the capacitance of the measuring equipment to be subtracted from the data; this value was .114 nF. The multimeter was then connected in parallel across the sample.

The set value of the temperature on the Omega Controller was set to 60 degrees using the "Index" button and arrow keys. To heat the sample, the variac dial connected to the heating coil was turned from 0 to 40 volts. The slowly rising temperature of the sample was displayed as the present value (PV) on the Omega Controller. One person can get the readings of the sample temperature while another records the corresponding capacitance values of the sample from the multimeter.

Let the sample temperature and capacitance go through one cycle to see where to expect rapid changes (where the Curie temperature is). Recording the capacitance values every couple of degrees was sufficient until 40 degrees, where measurements were taken every degree up to 47 degrees Celsius. Here measurements began being taken every 0.1 degree since this was the area in which the capacitance changed rapidly. Measurements were taken every 0.1 degree up to 50 degrees Celsius, where they were taken every degree again until reaching 57.5 degrees. Here it was determined that enough data had been collected and the heater was turned off by turning the voltage to zero.

The same procedure for collecting capacitance and temperature values was repeated as the sample cooled from 57.5 degrees to 20 degrees Celsius; however, during this decrease in the temperature, the capacitance values changed much more rapidly and this data acquisition method was very inaccurate with either one person or two people attempting to read the quickly changing measurements.

Temperature Dependence of Spontaneous Polarization, P_s:

The spontaneous polarization was measured using an electrometer to measure the charge on the conducting electrodes on the surface of the sample. In order for the charges on the faces of the sample due to polarization to be observed, the sample must be in a single-domain state (all the polarization must point the same direction in the crystal).

The sample chamber was cooled with ice water and at the same time the temperature was set to 54 degrees Celsius and the heating coil turned on. Once at 54 degrees (normal state), a DC power supply connected across the sample (from "S" to "D") was used to slowly apply a voltage of 50 volts. The power supply used was a Harrison 6274A, Hewlett Packard. With the power supply connected, the heater was turned off and the sample was allowed to cool to 13.5 degrees. The power supply voltage across the sample was then turned down from 50V to 0V and disconnected from the sample.

The sample was shorted out by connecting a single wire with banana plugs on both ends to "S" and "D" across the sample and left to sit for one minute. Now the sample should be in a single-domain state and the appropriate charge should be able to be measured. A Keithley 610B electrometer was then connected in series to the sample to measure the amount of free charge flowing from one side to the other as the sample was heated from 13.5 degrees to 54 degrees. The electrometer was zeroed before use by pushing the "zero" button.

The free charge reading on the electrometer was recorded as a function of the sample temperature. The electrometer sensitivity was set on the "10^{-7} Coulomb" scale. The 10 scale (on the display) was used for most of the electrometer measurements and had an uncertainty of +/- 0.1 (x 10^{-7} C). A few measurements at low temperatures were made using the 3 scale, which we found to have an uncertainty of +/- .05 (x 10^{-7} C).

Electrometer readings were taken every degree, then every 0.5 degree starting at 41 degrees. Between 48 and 49 degrees, measurements were recorded every 0.2 degree.

Hysteresis Loop Measurement:

The sample with capacitance C_s is connected in series with a reference capacitor of much larger value, C' (C'=50nF, C_s=0.1nF). Both of these are connected to a function generator and an oscilloscope as shown in the diagram above. Most of the voltage from the function generator applied from "D" to "G" goes to the sample since it has the smallest capacitance. Therefore, the total voltage V_t applied between "D" and "G" is proportional to the electric field, E, in the sample when the sample is at least a few degrees from the transition temperature.

The voltage V' applied across the reference capacitor between "S" and "G" is proportional to the displacement vector, D, in the sample.

The total voltage V_t is connected to CH 1 on the Tektronix 2205 oscilloscope, corresponding to horizontal deflection. The voltage V' connects to a unit-gain isolation amplifier, the output of which goes to CH 2 of the oscilloscope for vertical deflection. The amplifier must be used because the voltage-measuring device (oscilloscope) needs to have a larger impedance than the capacitor so it does not alter the signal you are reading. This provides a measure of D versus E, the hysteresis loop for the sample. A sawtooth waveform was set for the function generator; it was also set to .100 kHz and a peak to peak amplitude of 20V was used.

The waveforms shown from both channels on the oscilloscope are shown separately as well as plotted together in a hysteresis loop using a PC-based data acquisition system. V_t and V' are connected to ACH0 and ACH1, respectively, on BNC-2090 and the thermocouple is also connected to BNC-2090 through ACH2. BNC-2090 is then connected to the computer. For this program, the sampling frequency was set to 25000 because above this value, the program wouldn't work. This value divided by the 100 Hz from the function generator gives 250, the number of data points per waveform. "Number of data points shifted" was set to -1. The wait time was set to 1 second and it sampled for 10 ms. Thus, D vs. E hysteresis loops are generated every second for whatever the current value of the temperature is at that moment.

Very good descript

The sample started at 50.6 degrees and cooled to 39.5 degrees, at which point sufficient data had been obtained.

Results and Analysis

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Temperature Dependence of Dielectric Constant:

As discussed earlier, the dielectric constant was measured indirectly by measuring the capacitance of the sample as the temperature changed. The multimeter used to measure capacitance had an estimated error of +/- .001 nF. On the plots of capacitance versus temperature and (1/C) versus temperature, error bars were used with the value of +/- 1%. This percentage is rounding up from the .2-.6% error obtained from the estimated value of +/- .001 nF, but 1% is probably a realistic value for the error. The measurements from the multimeter can be inaccurate due to the capacitance of the measuring equipment itself—the capacitance of the three foot cord may be around 30 pF/ft, and the connectors have capacitance, etc. To correct for this error as best as possible, capacitance was measured using this multimeter with no source to get the "background" capacitance reading and this value (.114 nF) was subtracted from all of the data points.

Excellent!!

Figure 1 shows the inverse of the capacitance versus the temperature of the ferroelectric sample. The theoretical equations predict that near the Curie temperature on this plot, the line corresponding to $T < T_c$ should have a slope that is twice the value of the slope for the line corresponding to $T > T_c$. The experimental data presented here shows the slope for $T < T_c$ to be 2.46 times the slope for $T > T_c$. This represents a difference of 23% from the theoretical value. The slopes were calculated using data points within 2 degrees on either side of the Curie temperature, where the points seem to be arranged quite linearly. Perhaps the theoretical value of the ratio of the slopes would be obtained more accurately by fitting lines to more data points on either side of the Curie temperature and comparing the slopes of the fitted lines.

2.46 is actually correct value. The simple theory is not quite right.

The Curie temperature resulting from this data was found to be 48.2 degrees Celsius, the temperature corresponding to the highest value of capacitance. This capacitance maximum can be seen on Figure 2.

A trial involving measuring capacitance while lowering the sample temperature from 57.5 degrees to 20 degrees was discarded because the values of capacitance were changing so rapidly that the data was unreliable. There was not enough time to physically observe and record capacitance values and their corresponding temperature values near the transition temperature, and as a result, some values were missing or possibly mismatched. From the data obtained, however erroneous, this discarded trial gave a Curie temperature of 49.6 degrees Celsius. This raises an important point though—data is fluctuating rapidly near the transition temperature in this part of the experiment and therefore some operator error in reading the rapidly changing values may be present.

Temperature Dependence of Spontaneous Polarization:

Figure 3 attached shows the relationship obtained between the charge due to polarization in the sample and the quantity $\sqrt{(T_c - T)}$.

To obtain this data, the temperature was measured with the thermocouple as usual. To measure the spontaneous polarization of the sample, the charge freed by the disappearance of the spontaneous polarization is the quantity that is actually measured using an electrometer connected in series with the sample. As the polarization decreases, the free charge increases. Since the spontaneous polarization is zero at the transition temperature, the free charge measured at this temperature represents the initial free charge on the conducting electrodes. The charge measured at each temperature T was subtracted from this value to obtain the charge due to the polarization. Hence, the point at the origin of Fig. 3 corresponds to the Curie (transition) temperature and the other points correspond to temperatures lower than the Curie temperature.

The Curie temperature, the temperature at which the measured free charge was a maximum, was observed to be 48.5 degrees Celsius using this method.

The electrometer used to obtain the charge data had an estimated error of +/- 0.1 $\times 10^{-7}$ C. This error refers to uncertainty in reading the display, which is a scale with a deflecting pointer and it is only calibrated for reading to a certain degree of accuracy. This error value is what was used for the error bars on Fig. 3. The uncertainty estimated for some of the lower temperature values was only +/- .05 $\times 10^{-7}$ C because the 3 scale on the display was used for these values and seemed to have a smaller uncertainty. However, since most values used the 10 scale associated with the former value for uncertainty, the error bars were made to use this value.

Figure 3 would theoretically be a linear plot since P_s is directly proportional to $\sqrt{(T_c - T)}$. As seen from the figure, the plot becomes reasonably linear at a certain temperature. This temperature is 36 degrees Celsius and at temperatures below this temperature, the experimental data obeys the theoretical prediction, becoming very linear. This could be due to the fact that as the temperature gets very low, the sample is more strongly polarized.

Hysteresis Loop Measurement:

From the many plots of D vs. E generated by the computer program, an attempt was made to find the plot with the steepest slope. This plot would correspond to the hysteresis loop measured at the transition temperature since the slope of the plot corresponds to the dielectric constant, which is a maximum at the transition temperature. Three plots seemed to have high values for slope: the plots for 47.5 degrees Celsius, 48 degrees and 48.2 degrees. These slopes were roughly calculated to be, respectively: .28, .30, and .25. These slopes were roughly calculated using 2 points on each plot. Since the calibrations on the axes are not very detailed, the locations of these points had to be estimated and therefore there is enough uncertainty in these calculations that perhaps any of these three plots corresponds to the transition temperature. These estimated points are labeled on the three attached figures. The calculations suggest that the transition temperature occurs at 48.0 degrees Celsius.

Although there is some uncertainty in calculating the slope of these plots using the method I have discussed here, there may be an easier way of getting the slope from the computer program used to create the plots. There may have been available a more accurate way to calibrate the axes or maybe even part of the program that would calculate the slope. Unfortunately, we were unfamiliar with the intricacies of the computer program and could not find a more accurate method for obtaining the slope.

Discussion

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The ferroelectric triglycine sulfate (TGS) proved to be a good material to use for this experiment; its ferroelectric properties were easily observed. Observing various changes in the properties of the material under different conditions did fulfill the goal to better understand ferroelectric materials and ferroelectricity.

By measuring the temperature at which the TGS sample had the highest dielectric constant (highest capacitance), the experimental value of the Curie temperature was first obtained to be 48.2 degrees Celsius. This is reasonable since the known Curie temperature is said to be about 50 degrees Celsius. In addition, the plots produced (Fig. 1 and 2) significantly resembled the theoretical plots.

The temperature dependence of the spontaneous polarization of the TGS sample was obtained and compared to the theoretical relationship between spontaneous polarization and temperature. The proportionality of P_s to $\sqrt{(T_c - T)}$ is evident in Fig. 3 and the linearity is greatly increased at temperatures lower than 36 degrees, which can be expected.

Measurements of the electric field and the displacement vector in the sample were used along with a computer program to produce hysteresis loops at various temperatures. Finding three plots with the steepest slopes was easy, but the actual calculation of the slopes of the curves on these plots was not very precise due to lack of detailed (precise) calibration on the axes. Therefore, the Curie temperature obtained from this method was somewhere between 47.5 and 48.2 degrees Celsius; calculations suggested it was 48.0 degrees. The theory behind the hysteresis loops could still be understood and the Curie temperature found with this method does compare agreeably with other values; perhaps in the future there will be either an improved computer program or improved understanding of the computer program on my part to better use it to calculate the slope.

Altogether, the goals of this experiment were achieved within experimental uncertainties and the theoretical understanding of ferroelectricity was supported by the results obtained.

Conclusion

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The usefulness of computer data acquisition programs in lab environments is evident in this experiment. Gathering the hysteresis loop data using the computer and then analyzing the plots produced by the program provided much more accurate data and much more data than it would have been possible for a person to obtain by direct observation in many instances. However, one must be able to interpret the data acquired with some ease and precision in order for the technology to truly fulfill its potential.

References and Acknowledgments

1) Lab manual for "Ferroelectricity" lab provided in Physics 122 class at U.C. Davis

2) Griffiths, David J. *Introduction to Electrodynamics*, 3rd Edition. Prentice Hall, Upper Saddle River, New Jersey: 1999.

Fig. 1 (1/C) vs. T for Ferroelectric Sample

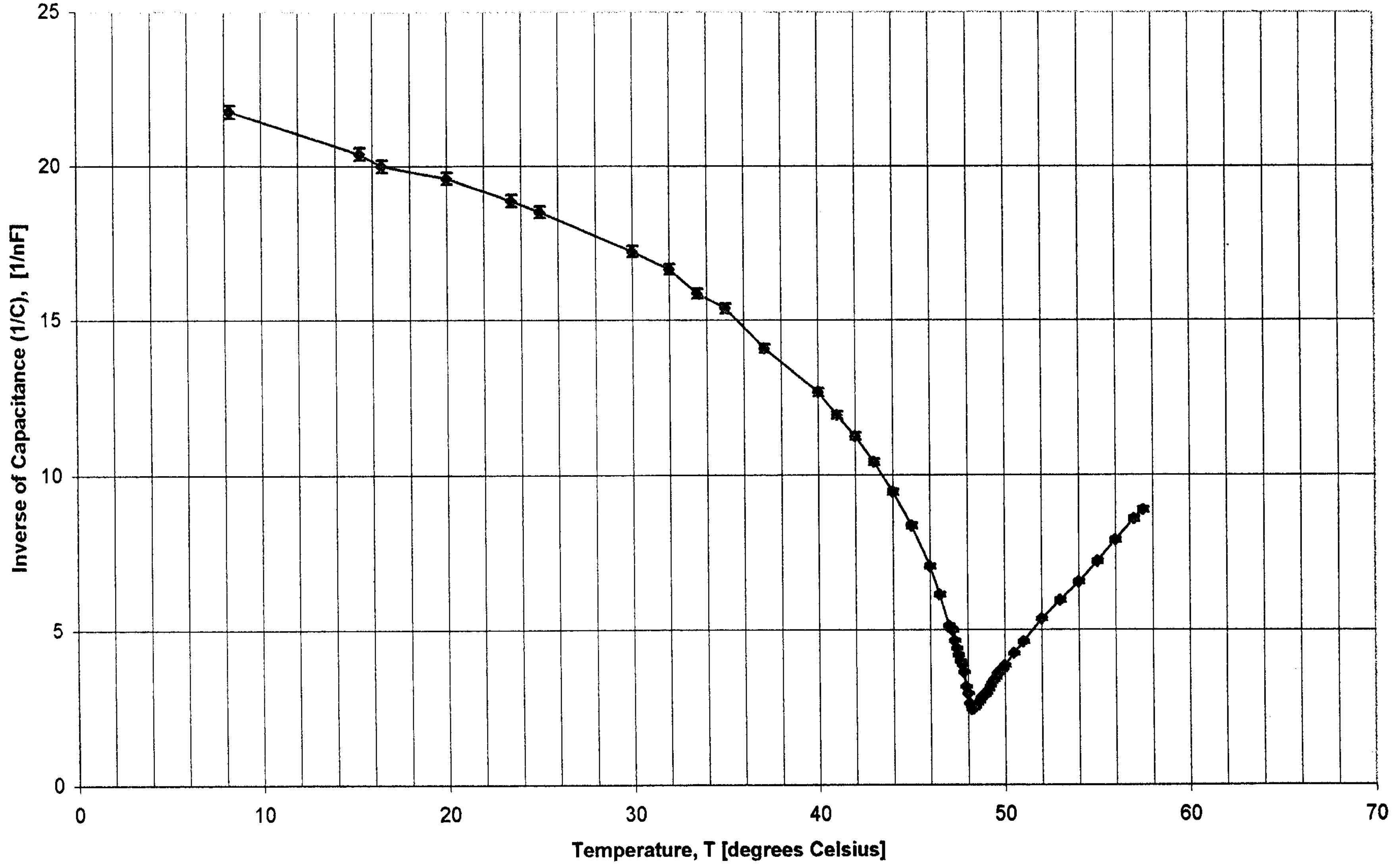


Fig. 2 C vs. T

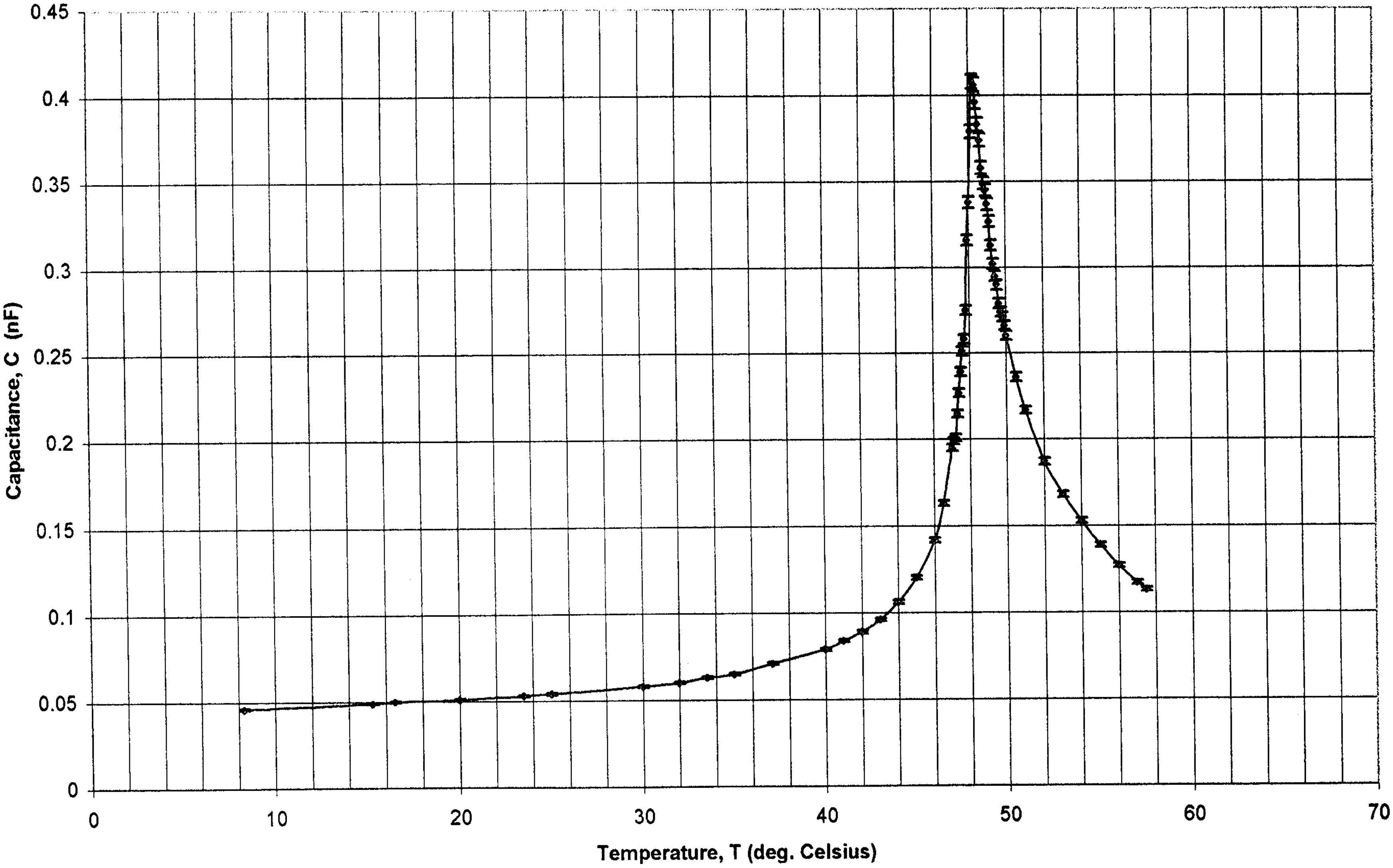
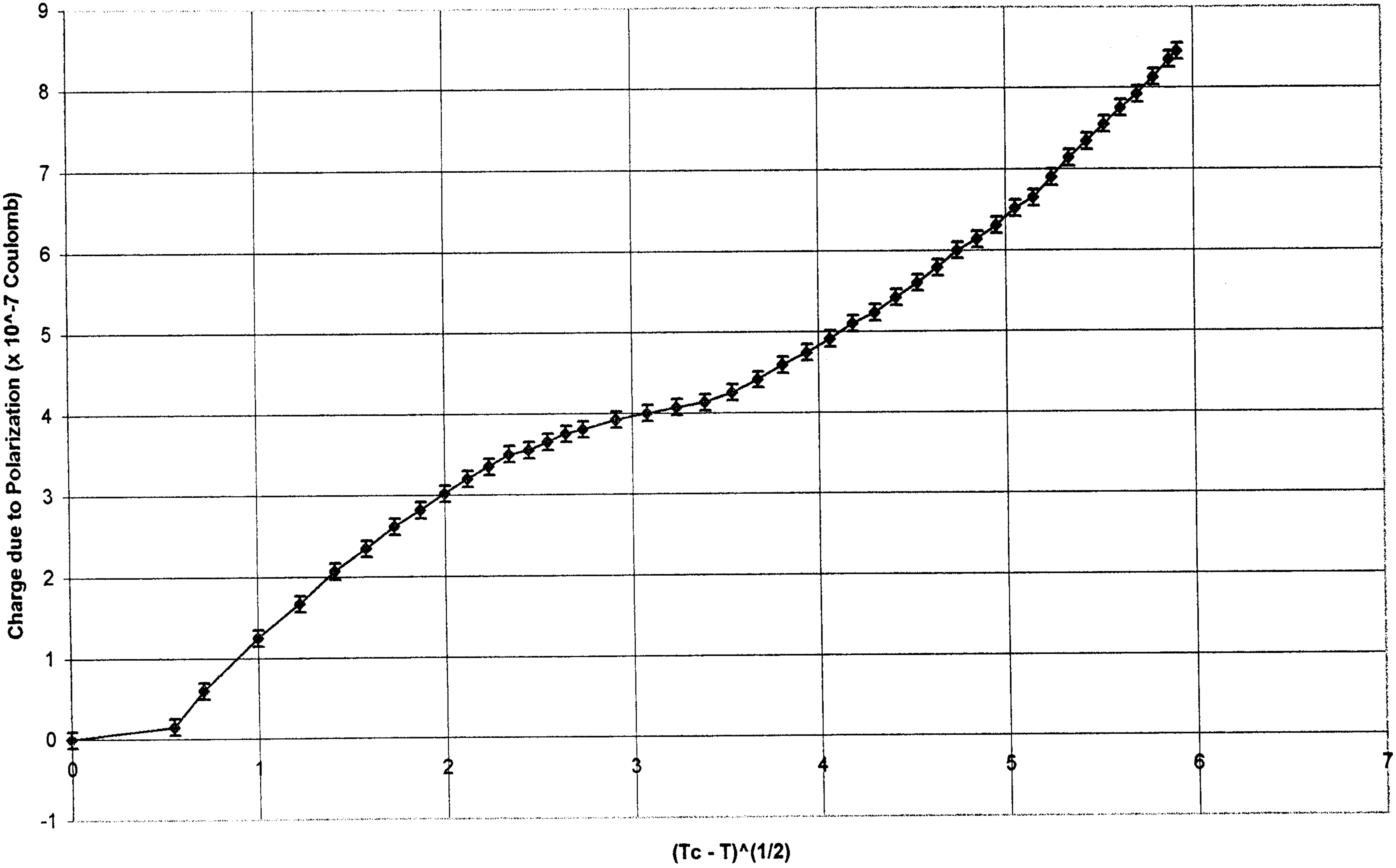
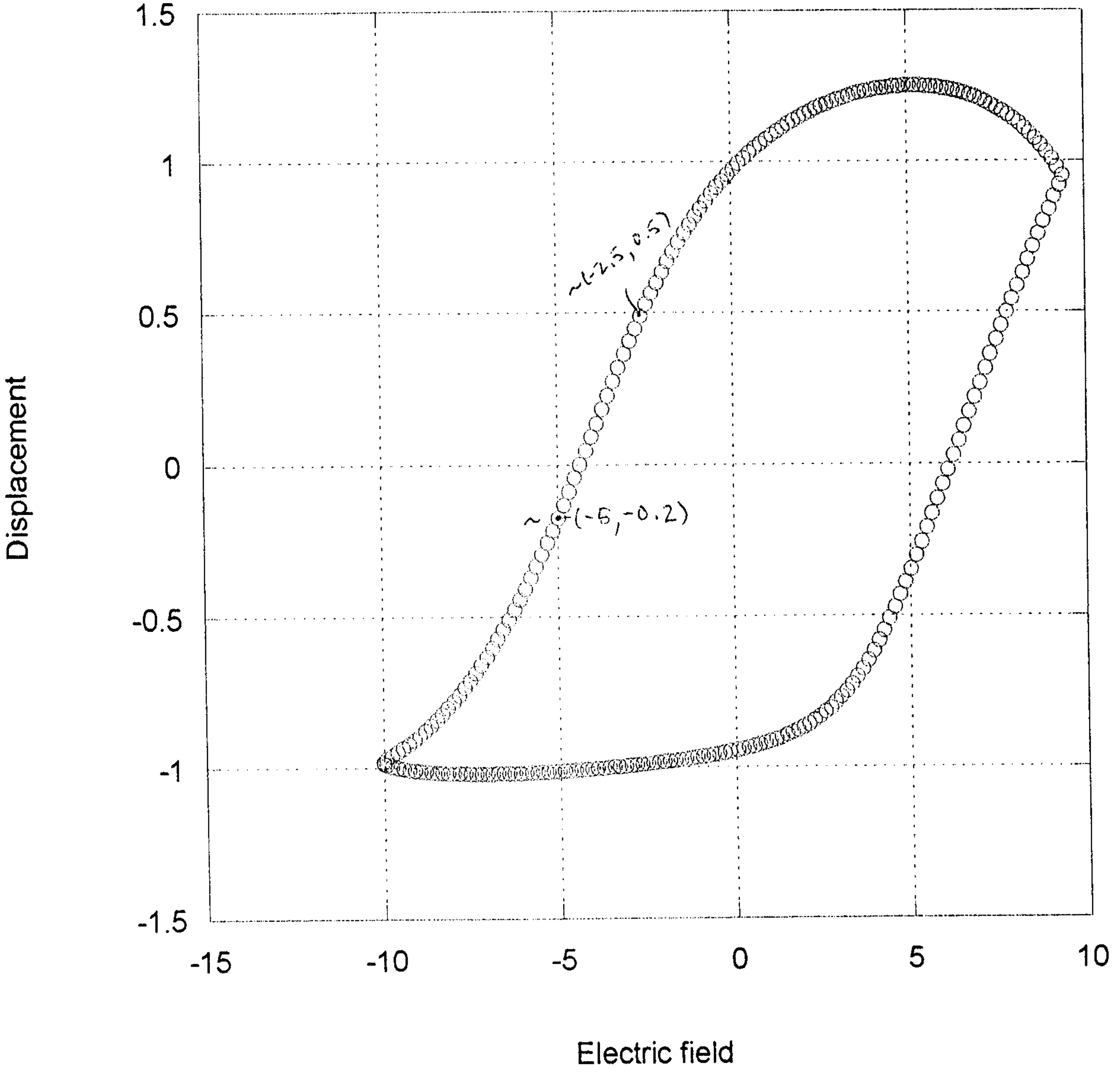

Capacitance, C (nF)
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
10
20
30
40
50
60
70
Temperature, T (deg. Celsius)

Fig. 3 Charge due to Polarization (Ps) vs. (Tc-T)^(1/2)

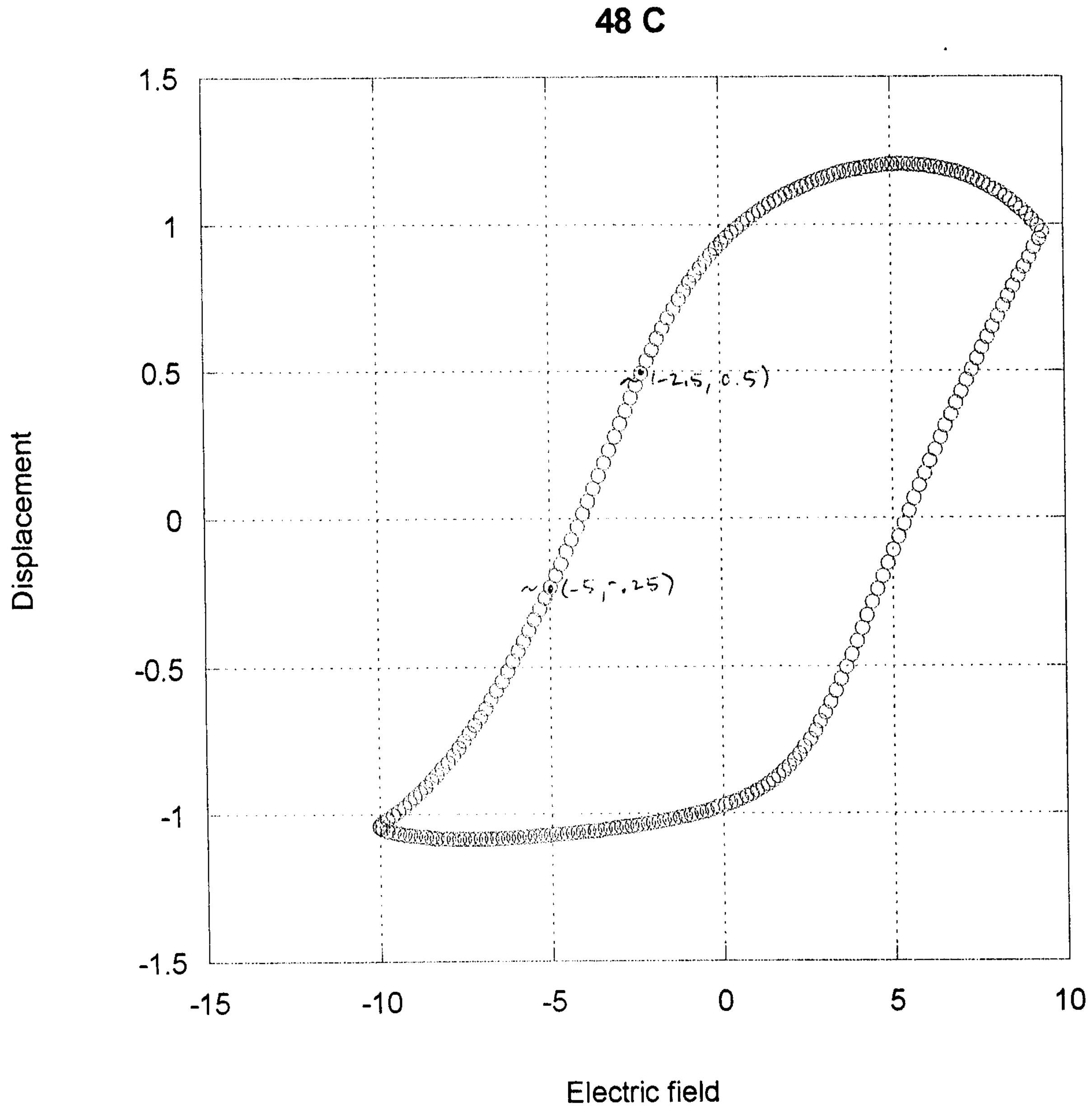


47.5 C



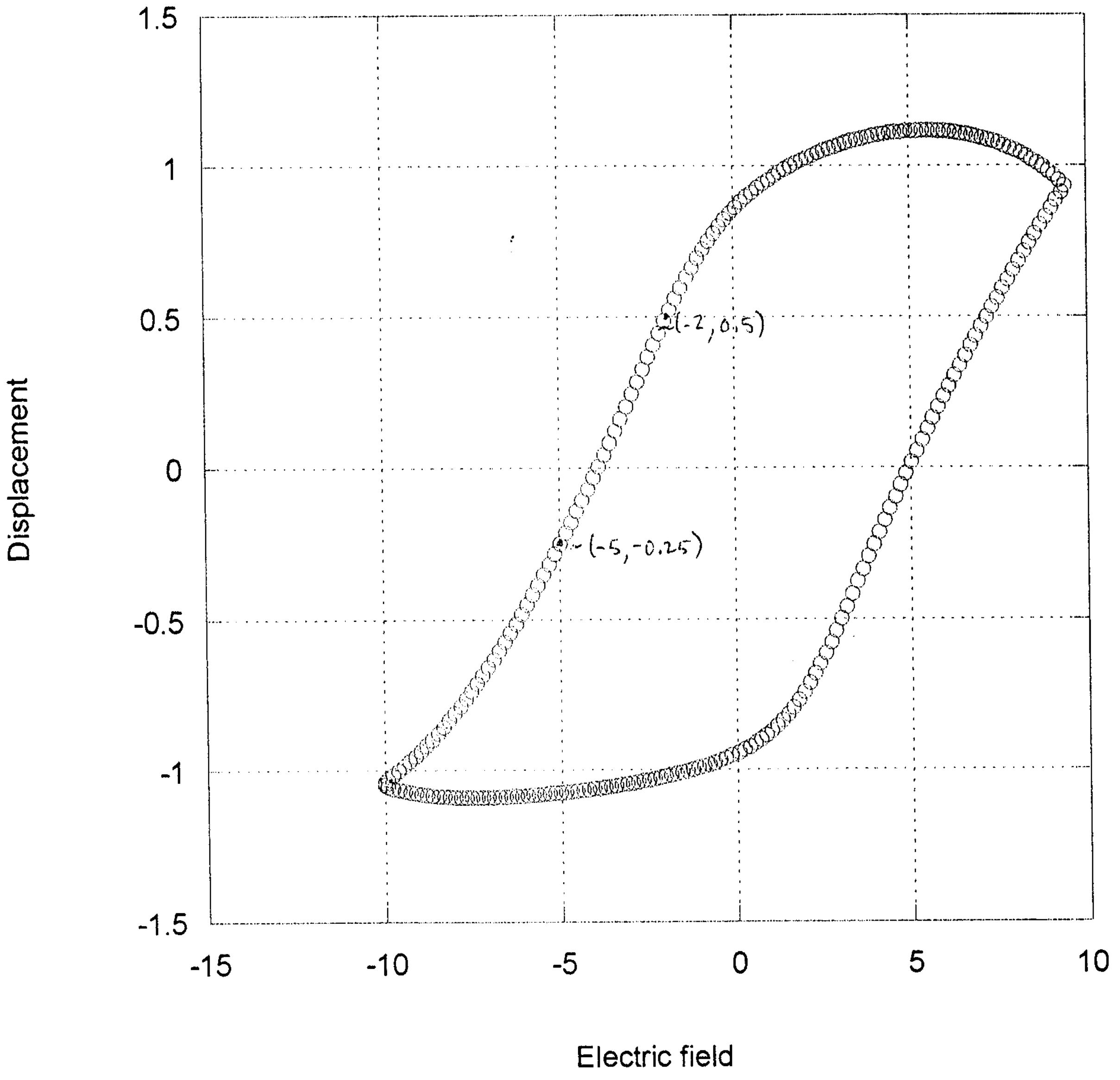
1.5
1
0.5
0
-0.5
-1
-1.5
-15
-10
-5
0
5
10
Displacement
Electric field
~(-2.5, 0.5)
~(-5, -0.2)

m ≈ .28


48 C
Displacement
Electric field
1.5
1
0.5
0
-0.5
-1
-1.5
-15
-10
-5
0
5
10
~(-2.5, 0.5)
~(-5, -.25)

m ≈ .30

48.2 C


1.5
1
0.5
0
-0.5
-1
-1.5
Displacement
-15
-10
-5
0
5
10
Electric field
(-2, 0.5)
(-5, -0.25)

m ≈ .25