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THE DIELECTRIC PROPERTIES OF THALLIUM NITRATE

BY

GENE E. GOWINS

A
THESIS
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ABSTRACT

The purpose of this research was to investigate the dielectric behavior of thallous nitrate and to determine whether it belongs to space group Pbnm or to Pbn2.

The growing of single crystals of thallous nitrate which are suitable for dielectric measurements is difficult because the crystals are prone to initiate a dendritic growth habit. In the present work single crystals of thallous nitrate were obtained, however, by slow evaporation of an aqueous solution at 55 degrees centigrade. The crystals were plates, not larger than 8 x 8 x 2 mm, whose principal faces were subsequently indentified as (001) planes. The plates were subjected to x-ray analysis to determine crystal orientation, and then shaped for dielectric and piezoelectric measurements.

Ferroelectric characteristics were investigated by measuring the dielectric constants along the three axes at the transition point, and also, by searching for a dielectric hysteresis loop. The results indicate that thallous nitrate is not a ferroelectric.

No piezoelectricity was observed in these crystals. These results favor the assignment of thallous nitrate to the space group Pbnm.

ACKNOWLEDGEMENT

The writer wishes to express his sincere appreciation for the active interest and guidance extended to him throughout the course of this investigation by Dr. Robert Gerson, Professor of Physics at the University of Missouri at Rolla, Rolla, Missouri.

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INTRODUCTION

This study is concerned with investigations of the dielectric properties of thallous nitrate. These measurements can be useful in determining the structure of the material and also in understanding the interaction of the atoms with each other.

In 1950 Ferrari and Cavalca (1), who were the first to investigate the structure of the room temperature phase of thallous nitrate by x-ray diffraction, concluded that the structure belonged to the space group Pbnm. The work of Nye (2) shows that space group Pbnm corresponds to the point group mmm and the point group mmm is a member of a centrosymmetrical class. All crystals that have a structure in a centrosymmetrical class cannot exhibit piezoelectric properties.

The latest structural studies of thallous nitrate were made in 1962 by S.W. Kennedy and J.H. Patterson (3) at the University of Adelaide, South Australia. They investigated the room temperature form of thallous nitrate by x-ray diffraction and concluded that the space group was either Pbnm or Pbn2.

The space group Pbn2 corresponds to the non-centrosymmetrical class mm2. All non-centrosymmetrical classes of crystals may have piezoelectric properties, so that the work of Patterson and Kennedy (3) indicates a crystal structure of thallous nitrate which suggests that the room temperature phase might be piezoelectric. The purpose of this investigation was to resolve the question of the structure of the room temperature phase of thallous nitrate. The question to which space group thallous nitrate belongs was answered by growing single crystals of thallous nitrate and using the single crystals to search for piezoelectric activity. If single crystals had exhibited piezoelectric properties, then the space group would definitely have been indentified as Pbn2. If the crystals were not found to exhibit piezoelectric properties, either the piezoelectric properties of the crystals were too weak to detect, or thallous nitrate could be said to be non-piezoelectric and definitely belongs to the space group Pbnm.

The single crystals grown by Patterson and Kennedy (3) for structural studies were small, (less than one-half mm long) and needle-like in shape. Such crystals are of sufficient size and shape for x-ray anaylsis, but the requirements for electrical measurements are quite different.

The first problem was therefore to grow single crystals of thallous nitrate that would have a suitable habit and size with which to make accurate measurements of dimensions.

The second problem was to determine the exact orientation of the unit cell in the crystal. After the orientation of the unit cell was determined the entire crystal was shaped into an orthorhombic form corresponding to that of the unit cell.

The third problem involved measuring the crystal's dielectric constant as a function of frequency for the purpose of observing any possible piezoelectric activity (4).

The fourth problem was to measure the dielectric constant of the crystal along each of the three axes as a function of temperature (5), which was a means of investigating possible ferroelectric properties.

REVIEW OF LITERATURE

A. Historical

In 1957 Hinde and Kellet (6) investigated the unit cell and space group of thallous nitrate at room temperature. The unit cell dimensions were found to be a=6.22, b=12.32 and c=7.9 angstroms. The space group determined from systematic absences of lines in the x-ray pattern was found to be Pbnm. The space group found was in agreement with that determined by Ferrari and Cavalca (1).

For seed crystals Hinde and Kettel (6) used specimens received from Mess's British Drug Houses. After recrystallization of these crystals from aqueous solution, needle-shaped crystals were found in each case. One crystal was selected for examination from each batch. In the crystal as received, the c axis was found to lie along the length of the needle, while in the recrystallized specimen the b axis lay in this direction. The unit cell c dimension of the crystal from each growth habit, however, was found to be the same.

In 1937 Finback and Hassel (7) reported that structural changes take place at elevated temperatures. In 1962 Brown (8) made a further study of the thermal transformations of thallous nitrate by differential thermal analysis, optical microscopy, x-ray diffraction and measurements of electrical conductance.

It was confirmed that thallous nitrate has three stable forms between room temperature and the melting point (205° C). On heating, transformation temperatures were found to be III$\xrightarrow{76^\circ C}$II$\xrightarrow{146^\circ C}$I.

The results of x-ray diffraction indicated that form III is orthorhombic with unit cell dimensions a=6.31, b=12.30 and c=8.01 angstroms. Form II was found to be a hexagonal unit cell with a=10.47 and c=7.52 angstroms. A cubic unit cell was found for form I with unit cell dimensions a=4.3 angstroms.

Single crystals of form III grown from aqueous solution and having a needle-shaped habit were examined under a polarizing microscope. The crystals were anisotropic. At the III→II transformation the crystals retained their external shape. Form II was also anisotropic. At the II→I transformation the crystals become isotropic. It was found that form II could be cooled to room temperature, but a transformation back to III usually took place within about 12 hours. The rate of transformation was many times lower than the rate of the III→II transformation. Measurements of the electrical conductance were made under vacuum, and at the III→II transformation a sharp decrease in conductance was observed. In the first experiment the conductance decreased by a factor of 200. The conductance of a second sample, which had been maintained under vacuum for over a week, decreased only by a factor of 14 on being heated through the III→II transformation. These results suggest that the fall in conductance at this transformation is probably associated with the removal of moisture, and that in a perfectly dry sample little or no change would be observed. At the II→I transformation the conductance increased by a factor of 100. Rowland and Brown (8) have shown by nuclear magnetic resonance that the Tl^+ ion mobility in form I near the melting point is as high as in the melt. Therefore, it is suggested that the 100 fold increase in conductance at the II→I transformation is due to the onset of positional disorder of the Tl^+ ions. The results described suggest that the transformations between III and II, and between II and I are not of the same type.

Although the III→II transformation takes place readily, the II→III transformation is difficult to initiate and the rate of growth is comparatively slow. The III→II and II→III transformations involve fairly drastic structural changes, but the conductance changes in dry samples are small. On the other hand, the II→I and I→II transformations take place at approximately the same temperature, the two structures are simply related, and the changes in electrical conductance are large. The II→I transformations are therefore, probably of the order-disorder type. The electrical measurements suggest then that both forms III and II are ordered structures.

In 1962 J.H. Patterson (9) performed structural studies of thallous nitrate with crystals grown from aqueous solution. These were obtained as small biprisms with only 111 faces developed, or as needles on the b axis with 111 faces and 101 faces developed. As it proved impracticable to grind plates or spheres of suitable size, a needle-shaped crystal of average diameter about 0.007 cm was chosen. The dimensions of the orthorhombic unit cell were found to be a=6.28, b=12.3, and c=8.10 angstroms and the density corresponded to eight molecules per unit cell. No pyroelectric effect could be detected. The outcome of Patterson's work was that the structure III of $T\ell NO_3$ appeared to be of a type not previously reported, the space group being either Pbnm or Pbn2.

Also of interest in this investigation were the possible ferroelectric properties of thallous nitrate. An investigation for possible ferroelectric characteristics was made in 1962 by M. Meinnel and R. Client (10), who attempted to measure the dielectric constant of the powder form of thallous nitrate as a function of temperature. They found a slight change in dielectric constant at the transition temperature, and a dielectric constant value of approximately eight over the temperature range of 25° C. to 100° C. The change in the dielectric constant at the transition point observed by these workers does not indicate ferroelectric characteristics. The use of the powder form of thallous nitrate for dielectric constant measurements is considered to be quite inaccurate because it averages the dielectric constant for all orientations and includes air. To make accurate measurements of possible ferroelectric and piezoelectric characteristics of thallous nitrate one needs single crystals of suitable size and habit.

The largest plate-like single crystals of thallous nitrate ever grown were obtained by R. Newman and R. Halford (11). The crystals grown by these workers were obtained by slow evaporation of an aqueous solution at 55° C. and were orthorhombic plates, not larger than 10 x 10 x 2 mm. The crystals grown by Newman and Halford were not used for electrical studies, possibly because of excessive conductivity.

B. Crystal Growing

There are two general procedures of growing single crystals from aqueous solution (11). In both methods one suspends a seed crystal by a thread in a beaker containing the solution. In both methods of growing crystals, the first step is to prepare a solution that is saturated at the temperature at which the crystal will be growing.

In the "sealed-beaker method" one should slowly lower the temperature of the saturated solution, which will allow the seed to grow as excess solute crystallizes on it. In the other method, the "evaporation method", one starts with a saturated solution and permits it to evaporate slowly. The top of the beaker is covered with pieces of filter paper, both to reduce evaporation and to keep dust out of the solution. As water evaporates, the solution becomes supersaturated and the seed grows. Table 1 lists crystals which have been successfully grown to large size from aqueous solution. In general all of the crystals which have been successfully grown to large size from aqueous solution are much more soluble in water than thallous nitrate.

C. Dielectrics

Dielectrics differ from conductors in that they have few free charges which can move through the material under the influence of an electric field (12).

The dielectric behavior of a solid is strongly dependent on the type of lattice, the degree of molecular freedom, and the chemical structure.

The polarization of an originally uncharged dielectric is due to a relative displacement of positive charges in the direction of the applied external electric field (E) and negative charges in the opposite direction. The displacement of charges within atoms and molecules of a dielectric makes each atom or molecule a dipole with a particular moment p. The polarization vector P is the dipole moment per unit volume at a given point and is a macroscopic quantity. If p is the average dipole moment per molecule in a small volume and N is the number of molecules per unit volume, then

$$P = N\,p. \tag{1}$$

The electrical property of a dielectric that is usually measured in the laboratory is the absolute dielectric constant or permittivity (ϵ). The relative permittivity or dielectric constant is defined as $K = \frac{\epsilon}{\epsilon_0}$, where ϵ_0 is the permittivity of free space and ϵ the permittivity of the material. The dielectric constant may depend on temperature, pressure, and on the frequency of the applied electric field.

The relation between the electric field vector (E), the electric displacement vector (D) and the polarization vector (P) is given by

$$D = P + \epsilon_0 E. \tag{2}$$

The electric field vector E is a measure of the external

TABLE 1

Large crystals grown from aqueous solution.

Alums (13)	$KAl(SO_4)\cdot 12H_2O$,e.g.
Ammonium orthophosphate (14)	$NH_4H_2PO_4$
Ammonium orthasrsenate (14)	$NH_4H_2AsO_4$
Hydrogen iodate (15)	HIO_3
Lithium sulfate (16)	$Li_2SO_4H_2O$
Magnesium sulfate (17)	$MgSO_4\cdot 7H_4O$
Potassium orthophosphate (14)	KH_2PO_4
Potassium orthoarsenate (14)	KH_2AsO_4
Rubidium orthophosphate (18)	RbH_2PO_4
Sodium bromate (19)	$NaBrO_3$
Sodium chlorate (20)	$NaClO_3$
Sodium chloride (20)	$NaCl$
Sodium nitrate (21)	$NaNO_3$
Zinc sulfate (21)	$ZnSO_4\cdot 7H_2O$
Potassium sodium tartrate (22)	$KNaC_4H_4O\cdot 4H_2O$

field applied to the dielectric. The electric displacement vector is a measure of only the "free charges" in the dielectric, while P is a measure of only the "polarization charges". For linear isotsopic dielectrics E, P, and D have the same direction. For this particular case

$$D = \epsilon E. \tag{3}$$

This equation can be expressed in component form along three mutually perpendicular axes where each component of D is proportional to the corresponding component of E. In the case of anisotropic dielectrics the previous relations will no longer hold since in general ϵ will be different along different directions. In order to specify the dielectric constant of some material we have to specify in general nine coefficients, of which six are different. For the specific case of an orthorhombic system, three coefficients are needed to describe the relationship between the electric displacement vector and the electric field vector.

D. Ferroelectricity

The structures of some piezoelectric crystals are asymmetric in such a way that they are spontaneously polarized in the absence of an external field. The electric field produced by the permanent dipoles inside the crystal, however, is usually masked by charges on the crystal's surface. Since the polarization due to permanent dipoles present inside an insulator is temperature-dependent, a change in the temperature of the crystal produces a change in its polarization which can be detected. This is called the pyroelectric effect, and crystals belonging to ten out of the twenty piezoelectric crystal point groups exhibit this property. If it is possible to reverse the polarization direction of a pyroelectric crystal by applying a sufficiently intense external field, then the crystal is said to be ferroelectric. It should be noted that both piezoelectricity and pyroelectricity are inherent properties of a crystal, predictable entirely from its atomic arrangement of crystal structure. Ferroelectricity, on the other hand, is an effect produced in a pyroelectric crystal by the application of an external electric field (23), and is not predictable on the basis of structure.

The term ferroelectricity is applied to this phenomenon because it is quite similar to the phenomenon of ferromagnetism. Many ferroelectric crystals undergo a transformation at a certain temperature, frequently called the Curie point, above which, they are no longer polar even though they may still have non-centrosymmetric structures. The dielectric constant of these crystals increases without limit at these temperatures and, in general, behaves quite similarly to the Curie-Weiss law of ferromagnetism.

$$K_e = \frac{C}{T-T_c} + K_o \qquad (4)$$

where C is the so-called Curie constant, T_c is the transformation temperature, and K_o represents the contribution due to electronic polarization as distinct from the ionic contribution. When $T \cong T_c$, and $K_e >> K_o$, the electronic contribution can be neglected.

Ferroelectricity was discovered in 1920 by Valasek (24), when he obtained the first dielectric hysteresis loop and discovered the Curie temperature of Rochelle salt crystals at which the ferroelectric effect disappears. The following significant properties are associated with ferroelectrics (25)

a. They possess a dielectric hysteresis loop, indicating reversible spontaneous polarization.

b. They have a high dielectric constant, rising to a peak at the Curie point.

c. They possess a peusdosymmetric structure.

d. They possess symmetry which places them in a polar class.

e. They show disappearance of hysteresis at a certain temperature, the Curie point.

Of these, item (a) is characteristic of ferroelectrics and may be used to define them.

E. Piezoelectricity

The piezoelectric effect was discovered experimentally by the brothers Pierre and Jacques Curie in the year 1880 (26). By placing a weight on the surface of a crystal they produced a charge, measurable with an electrometer, which was proportional to the applied weight. This is called the direct effect. The converse piezoelectric effect, namely the production of a crystal strain when an electric field is applied, was predicted theoretically by Lippman in the following year and was verified by the Curies.

Crystals can be divided into 32 classes on the basis of the symmetry they possess. Of these 32 classes, 20 possess the property of piezoelectricity and 12 do not. The criterion that determines whether a crystal is piezoelectric or not is its possession of a center of symmetry. A crystal possessing a center of symmetry cannot be piezoelectric because no combination of uniform stresses will produce a separation of the centers of gravity of the positive and negative charges and cause an induced polarization.

Considering the effect of symmetry on the elastic and dielectric constants of the crystal, as well as on the piezoelectric constants, a crystal with no symmetry at all will have 21 different elastic constants, 18 piezoelectric constants, and 6 dielectric constants. As the symmetry increases, the number of possible different constants decreases. The most symmetrical type of crystal, a cubic crystal, has only 3 elastic constants, 1 piezoelectric constant and 1 dielectric constant (26).

If the space group of thallous nitrate is Pbnm then the point group is mmm, the crystal has a center of symmetry, and it cannot be a piezoelectric. On the other hand, if the space group of thallous nitrate is Pbn2, the point group is mm2 and the crystal does not have a center of symmetry and will be a piezoelectric.

The constants of the crystal vary depending upon the conditions of measurement. For example, if the dielectric constant of a crystal is measured when it is clamped so that it cannot move, the piezoelectric effect does not contribute and one obtains the so-called clamped dielectric constant of the crystal. If now the clamp has come compliance, some additional energy can be stored in the crystal in mechanical form, and this results in an increase in the dielectric constant. The effect is greatest when the crystal is free to move, and one obtains the so-called "free" dielectric constant (26).

EXPERIMENTAL PROCEDURE

A. Materials and Equipment

The materials and equipment used in growing the single crystals of thallous nitrate and measuring their dielectric properties are listed below.

(a) Mineral oil bath, Stirrer, Relay, Thallium Nitrate.

(b) Mercury thermostat, accurate within 0.02° C.

(c) Variacs, Synchronous motors.

(d) Hot plate, Beakers, Test tubes, Graduate cylinders, Filter paper.

(e) Glass rods, Epoxy, Aluminum oxide.

(f) Electric furnace, Chromel alumel wire, Potentiometer.

(g) Q-Meter (Model No. 260-A), Signal generator, Voltmeter.

(h) Schering capacitance bridge (GR Type 716-C).

(i) Traveling microscope, Stereo microscope.

(j) Acetone, Isopropyl alcohol, Urea, Methyl alcohol, Distilled water.

(k) X-ray apparatus.

(l) Vacuum pump, Oscilloscope.

The powder form of thallous nitrate was obtained from the Fisher Scientific Company, St. Louis Missouri.

B. Growing Crystals

The first step was to determine the solubility curve for thallous nitrate. A plot of solubility versus temperature is shown in Figure 1 (27).

The considerable change of solubility with temperature is favorable to growing of the crystal from aqueous solution. An apparatus was then prepared to use the "sealed beaker" crystal growing method (27). This method requires an automatic temperature dropping control, which was made by meshing a clock motor gear with a gear on the spindle of the thermostat. With the clock motor and the gear ratio employed, the bath temperature was dropped 1 degree centigrade every twenty-four hours. By changing the gear ratio the amount of temperature change per day could be accurately controlled. A photograph of the crystal growing apparatus is shown in Figure 2.

A solution of one hundred grams of distilled water and fifteen grams of thallium nitrate was heated in a sealed test tube to a temperature of forty degrees centigrade. Then a small amount of the solution was poured into a watch glass for the purpose of growing seed crystals. The remaining solution in the test tube was immersed in a water bath which was at a constant temperature of thirty degrees centigrade.

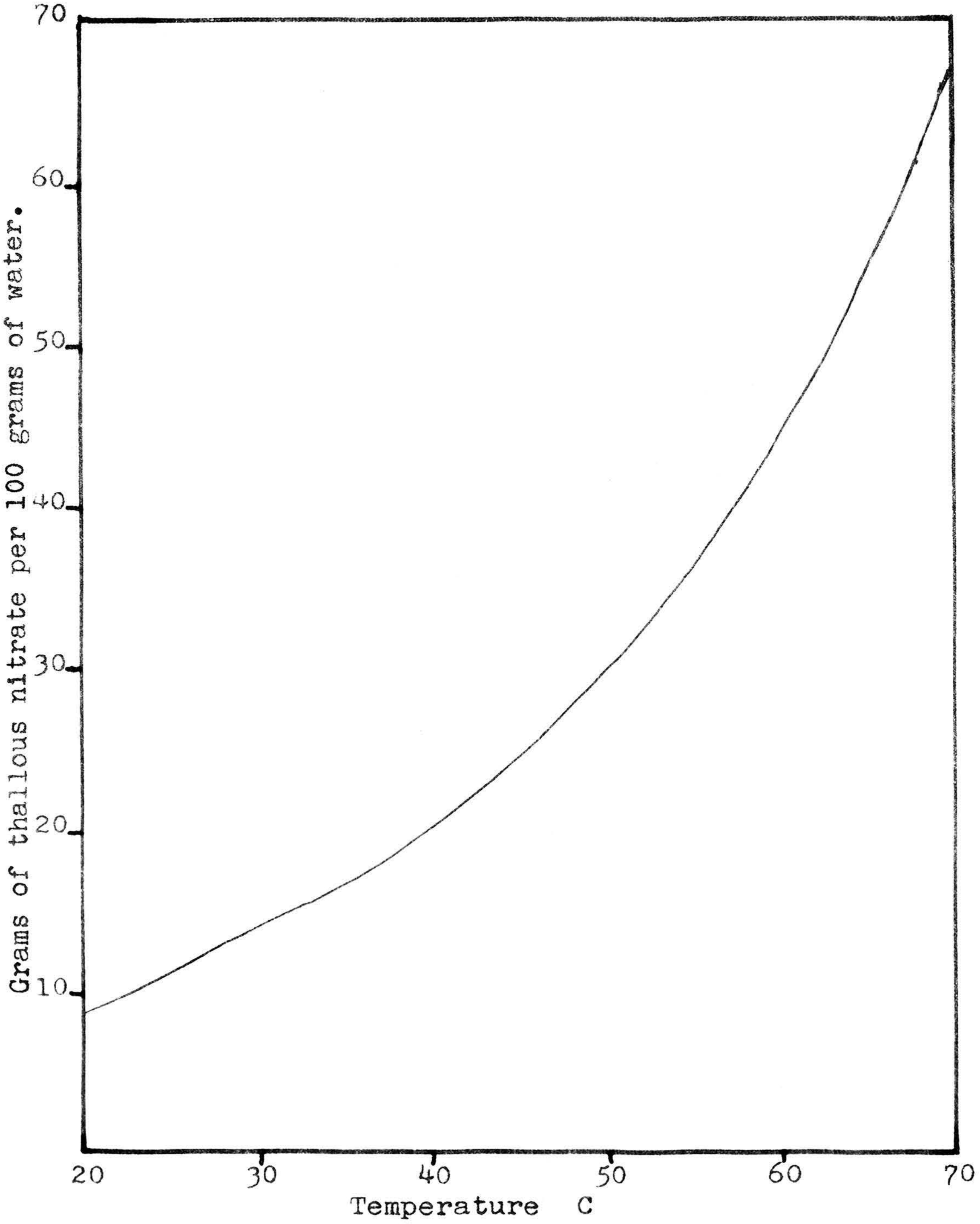

Figure 1. Solubility curve for thallous nitrate.

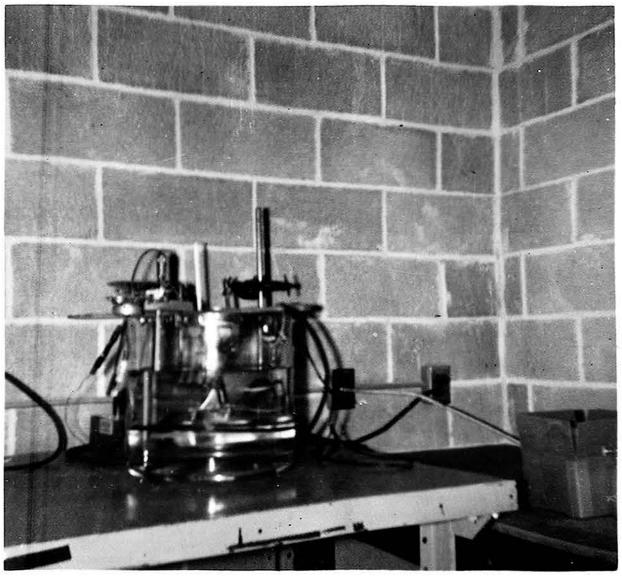

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Figure 2. Photograph of crystal growing apparatus.

After a few hours the distilled water evaporated from the watch glass, leaving some small needle like crystals. These were glued with epoxy resin to a fiber and placed under a lamp until the epoxy hardened. After the fiber attachment, the seed crystal was hung in the solution and density currents near the seed crystal were observed. If the density current was descending, extra thallium nitrate was being dissolved from the crystal and therefore the solution was unsaturated (27).

In the first attempt a descending current was observed. However, the seed crystal was left in the solution and the clock motor was activated with the hope that only a small portion of the seed would dissolve until the drop in temperature produced sufficient saturation to initiate growth. Many attempts, using this same method were unsuccessful and the method proved of little value. In each case the rate of seed crystal depletion was such that the seed always dissolved before the solution was saturated. The theoretical saturation point of the above solution was near room temperature. A new solution was prepared which placed the saturation point at a point on the solubility curve corresponding to a temperature of 35 degrees centigrade.

Again the seed crystal dissolved rapidly near the new theoretical saturation point. However, when the temperature was lowered to 33° C and a seed crystal inserted in the solution, very rapid crystallization would occur throughout the beaker. The seed crystal would develop into a series of long needles, advancing at rates observable by the eye, with gaps in between where practically nothing appeared to be happening.

Several attempts were made to start seed crystal growth in the temperature range between 33 and 35 degrees centigrade, but rapid dendritic growth would always predominate. It was also noticed that the solution formed a brown sludge at the bottom of the beaker. This was thought to be due to hydrolysis of a small amount of thallic salt present in the material. After heating the solution to boiling, and then filtering, this impurity was effectively removed. The resulting solution was again subjected to the same methods of crystal growth in the temperature range between 33 and 35 degrees centigrade, but the result was the same as before filtering. The same general method was used at other points along the solubility curve up to 50° C., with the resulting crystal growth always having a dendritic habit.

The next procedure was to design a method of rotating the seed crystal in the solution. This was accomplished by glueing the seed crystal to a glass rod which was attached to a synchronous motor. Again the same general methods as previously described were tried using 5 different theoretical saturation temperatures between 30 and 50 degrees centigrade, but the crystal's growth habit was not changed.

At this point it was decided to add impurities to the solution hoping to modify the crystals external shape. The best known example of habit modification is the influence of urea on sodium chloride (28). Sodium chloride crystallized from pure water solution in cubic form, but with urea added the crystals form octahedra. The habit modification is probably caused by the adsorption of foreign atoms or molecules along preferred crystal planes, which prevents growth on these planes. Such modifiers have found practical use in growing ammonium dihydrogen phosphate in a perferred direction (29).

The impurities added to the solution of thallous nitrate were acetone, isopropyl alcohol, urea, methyl alcohol and nitric acid, with crystallization being observed near 30, 40, and 50 , degrees centigrade. However, there was no observable change in habit.

At this state of the investigation the "evaporation method" was resorted to (30). It was found that while a solution of thallous nitrate and distilled water evaporated at room temperature is prone to initiate dendritic growths, this habit is broken by proceeding to

55° C. Orthorhombic plates, not larger than 8 x 8 x 2 mm, were obtained by placing 25 grams of solution in a 200 ml beaker, covering the beaker with 9 layers of filter paper, and holding the temperature constant at 55° C., allowing most of the solution to evaporate in 3 days. The plate like single crystals were difficult to grow because the proper rate of evaporation was hard to control.

C. Determination of orientation

Preliminary microscopic examination of the plates for orientation was inconclusive because the shapes of the plates were unfavorable.

Electrical measurements require placing the crystal in a holder and measuring dielectric properties along the three mutually perpendicular axes. The external shape of the crystal should conform with that of the orthorhombic unit cell. To obtain the proper crystal shape the orientation of the unit cells within the irregular crystal must be determined and the crystal shaped accordingly.

The orientation was obtained by x-ray methods. A rotating-crystal method, in which a single crystal was rotated about a fixed axis in a beam of monochromatic x-rays was used (31). For a picture of the x-ray equipment used, see Figure 3. The film was mounted with

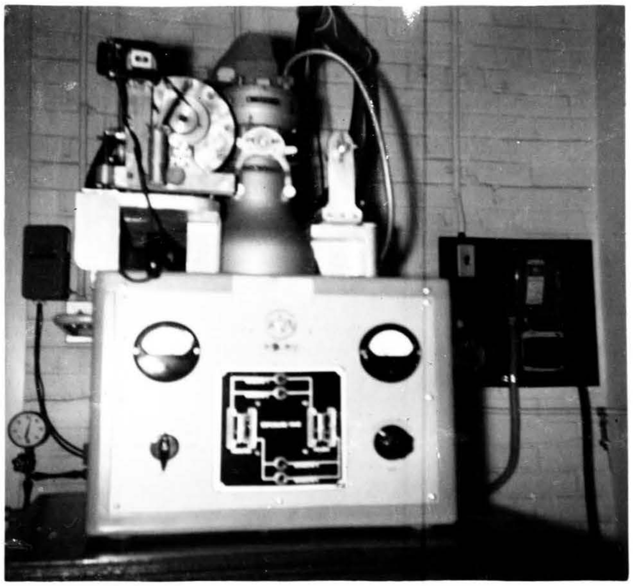

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Figure 3. Photograph of x-ray equipment.

cylindrical geometry concentric with the rotating spindle holding the single crystal.

The incident monochromatic x-ray beam is diffracted from a given crystal plane of interplanar spacing d whenever, in the course of rotation, the value of ϕ satisfies the Bragg equation (31). The symbol ϕ **denotes** the angle between the cylindrical axis of the camera and the line described by the x-ray reflections from the crystal. In particular, all planes parallel to the rotation axis will reflect in the horizontal plane. Planes with other orientation will reflect in layers above and below the horizontal plane. The crystal's alignment inside the camera may be adjusted by using a goniometer head. After adjusting the crystal in the camera so that one of the unit cell parameters is parallel to the cylindrical axis of the camera, one observes parallel dots on the developed film. For x-ray film prints of the thallium nitrate crystal see Figure 4.

The distance between any two consecutive rows of dots on the film was used to calculate the unit cell distance along the cylindrical axis by using the following relations:

$$\tan\phi = \frac{r}{h} \qquad \frac{\lambda}{\cos\phi} = x \tag{4}$$

where x = any one of the crystal's constants.

Figure 4. Prints of x-ray film. The top print is the pattern before crystal axis was aligned in the camera. The bottom print is the pattern when one of the crystal axes was parallel with camera axis.

r = radius of camera.

h = distance between any two consecutive lines on film.

ϕ = angle between cylinder axis and line described by reflections.

λ = wavelength of x-ray.

Since the crystal's principal faces are parallel, and the unit cell is orthorhombic, only two lattice constants must be evaluated for orientaion. For lattice parameter data calculated from the x-ray films, see Table 2. From the table one can see that the value of $h = 4.02$ mm calculated from the distance between consecutive lines on the x-ray film corresponds to the b axis lattice parameter.

After determining the unit cell orientation, the crystal was left on the goniometer head and shaped with emery paper into an orthorhombic form.

D. Ferroelectric Measurements

A ferroelectric type of crystal is one which exhibits a spontaneous polarization in one or more directions of the crystal over a definite temperature range. One phenomenon associated with a ferroelectric crystal is a wide variation of the dielectric constant of the crystal as a function of temperature. In this work the dielectric constant was measured as a function of tem-

TABLE 2

Lattice parameter data for thallous nitrate.

r mm	h mm	tan ϕ	ϕ	cos ϕ	λ	x
31.85	4.02	7.96	82.8	.1247	1.54	12.3
31.85	7.9	4.03	76	.240	1.54	6.3

From the table one can see that the measurements on the film correspond to the a and b axes.

perature along the three mutually perpendicular axes.

To measure the dielectric constant of thallous nitrate as a function of temperature it was necessary to construct a furnace. To eliminate stray capacitance effects short leads connected the Q-meter and the sample holder in the furnace. For a schematic diagram of the furnace, see Figure 5. The entire furnace was mounted on a Q-meter and by simple connections, the capacitance of the crystal could be measured at different temperatures. For a picture of the apparatus see Figure 6.

Since the dielectric constant as a function of temperature was to be calculated along the three mutually perpendicular axes, one must measure the capacitance along each axis as a function of temperature. The physical dimensions of the sample were measured and then by use of the relation

$$C = \frac{\epsilon_0 KA}{d} \qquad (5)$$

Where C = Capacitance of sample,
= Permittivity of free space,
A = Electroded area of one side of sample,
d = Thickness of sample,
K = Dielectric constant.

The values of the dielectric constant along the

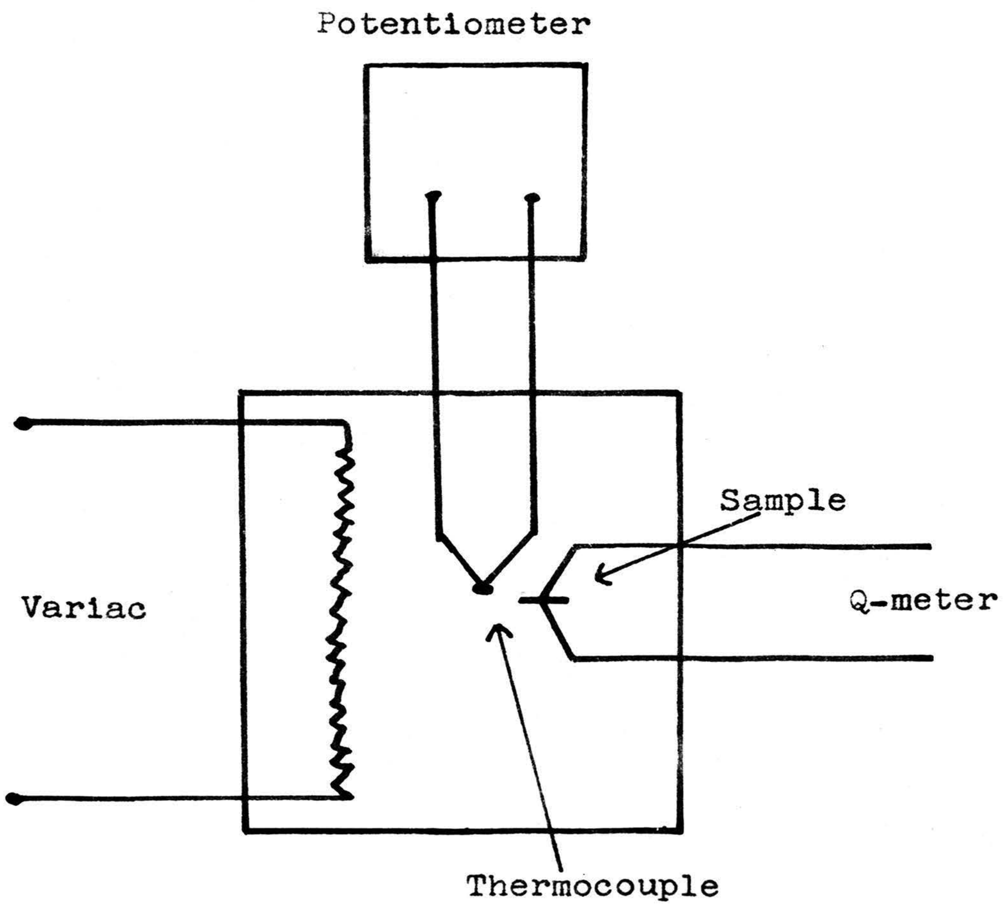

Figure 5. The schematic diagram of the furnace.

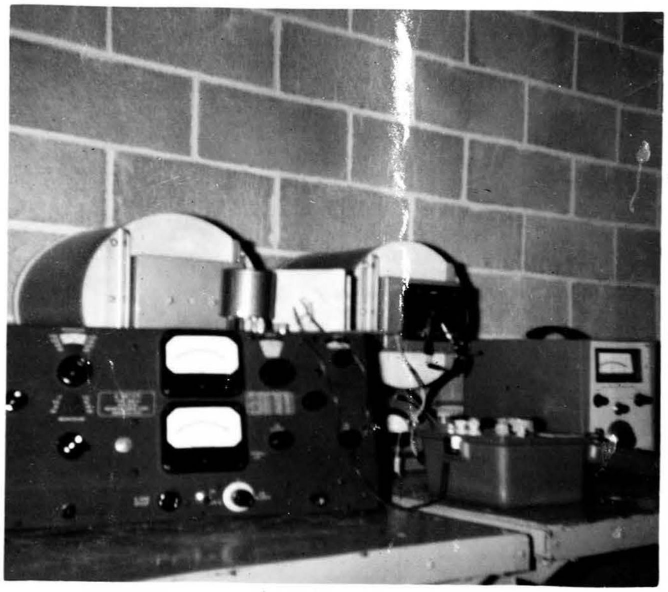

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Figure 6. Photograph of capacitance bridge and furnace.

three axes were determined. The dielectric constant along each axis was corrected for fringing effects caused by curving flux lines in air from one electrode to the other. The relations used for correcting the fringing effect are given as follows (32).

$$K = \frac{C_x - C_e}{C_a} \tag{6}$$

where C_x = The measured capacitance,

C_a = The interelectrode capacitance,

C_e = The edge correction,

For flat opposing parallel plates (32).

$$C_a = 0.08854 \frac{A}{d}, \text{ when dimensions are in cm.,} \tag{7}$$

$$C_e = (M + N)\ P \tag{8}$$

where M = $0.058 \log \frac{1.5}{d}$ when the dimensions are in cm.,

N = 0.0185 when the dimensions are in cm.,

P = Distance around the perimeter of the electrode,

A = Area of one plate,

d = Thickness between the two electroded faces.

In initial attempts to measure the capacitance of a sample a very large dissipation factor was observed. The high dissipation factor (20 per cent) was thought to be due to moisture within the crystal. In an attempt to remove the moisture the sample was placed in a desiccator and left for 24 hours. However, only a small drop in dissipation factor was evident after trying this drying method.

The next step involved heating the sample at a temperature of 55 degrees centigrade for a period of 12 hours. Again there was only a slight drop in the dissipation factor. Since it was impossible to heat the sample above 76 degrees without possibly destroying its single crystal character, the crystal was placed in a vacuum chamber and maintained at a pressure of one micron for 4 hours at room temperature. Again the dissipation factor showed little change. Finally the sample was heated to a temperature of 55 degrees centigrade at a pressure of one micron. Using the method of simultaneous heating and pumping, and carefully handling the sample afterwards, the dissipation factor was lowered to a value of less than 2 per cent when measured at a frequency of 1 kilocycle, and less than 1 per cent when placed in a 1 megacycle field. This procedure apparently solved the problems caused by excess moisture.

The first measurements made on the samples were an attempt to determine piezoelectric properties (see page 41). Then the dielectric properties were measured. An oriented sample of dimensions 4.20 x 3.30 x 1.84 mm was placed in the Q-meter circuit and its capacitance along the c-axis was determined as a function of temperature. The dielectric constant measured along the c-axis had a value of approximately 16 over the temperature range from 25° C. to 100° C. There was no significant change in the dielectric constant along the c-axis at the transition temperature. Silver electrodes were painted on the two smaller samples for the purpose of measuring the dielectric constant, along the a and b axis. For a picture of the crystals cleavage orientation, see Figure 7.

After determining the capacitance of each of the three samples as a function of temperature, the dimensions of each sample were measured with a traveling microscope. The equation (6) was used to calculate the dielectric constant along each of the three axes as a function of temperature. For capacitance versus temperature data, see Table 3.

When equation (8) was used in calculating the dielectric constant, the edge correction capacitance was approximately ten per cent of the measured capacitance. For a graph of the dielectric constant versus temperature along each of the axes, see Figure 8. The graph of the dielectric constant versus temperature indicates that thallous nitrate is not a ferroelectric, since the dielectric constant is relatively constant near the transi-

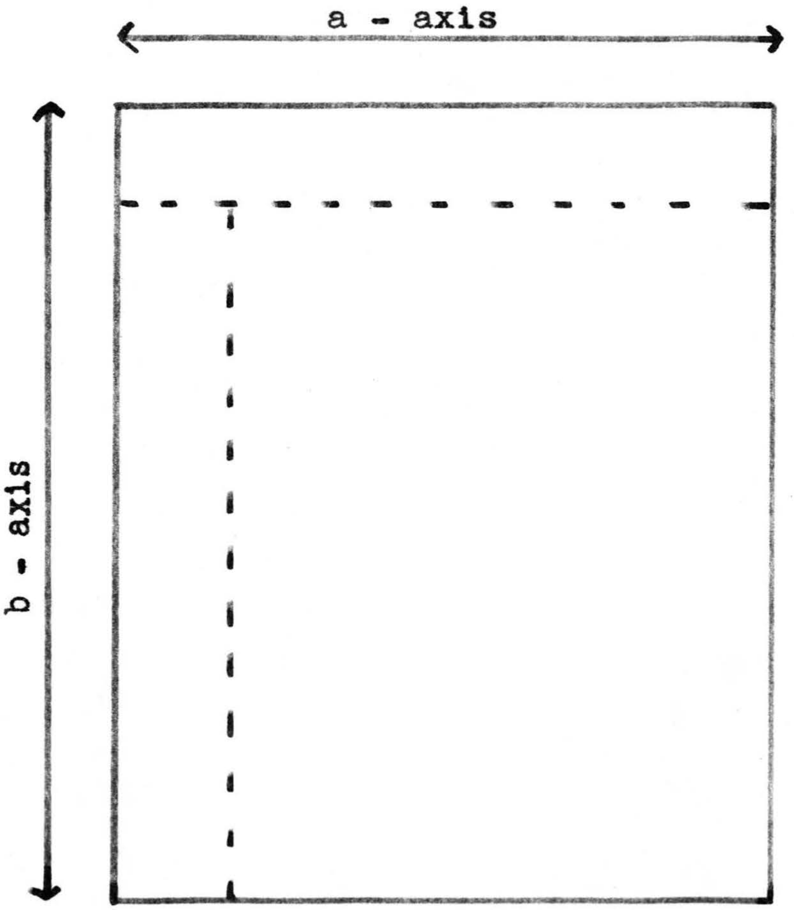


Figure 7. Drawing of crystal cleavage

TABLE 3

Capacitance vs. temperature data for thallous nitrate.

a-axis Crystal Dimensions 4.65 x 1.50 x 1.64 mm

Capacitance mmf	Dielectric Constant	Temperature C.
0.90	19.5	25
0.90	19.5	32
0.90	19.5	40
0.92	19.6	47
0.92	19.6	55
0.92	19.6	62
0.94	19.7	70
0.94	19.7	77
0.96	19.9	85
0.96	19.9	92
0.96	19.9	100

b-axis Crystal Dimensions 3.20 x 1.50 x 1.84 mm

Capacitance mmf	Dielectric Constant	Temperature C.
0.70	18.5	25
0.70	18.5	32
0.70	18.5	40
0.72	18.6	47
0.72	18.6	55
0.72	18.6	62
0.74	18.8	70
0.74	18.8	77
0.78	19.1	85
0.78	19.1	92
0.78	19.1	100

TABLE 3 - (continued)

c-axis Crystal Dimensions 4.20 x 1.84 x 3.20 mm

Capacitance mmf	Dielectric Constant	Temperature C.
1.15	16.4	25
1.15	16.4	32
1.18	16.5	40
1.18	16.5	47
1.18	16.5	55
1.18	16.5	62
1.18	16.5	70
1.20	16.7	77
1.20	16.7	85
1.20	16.7	92
1.20	16.7	100

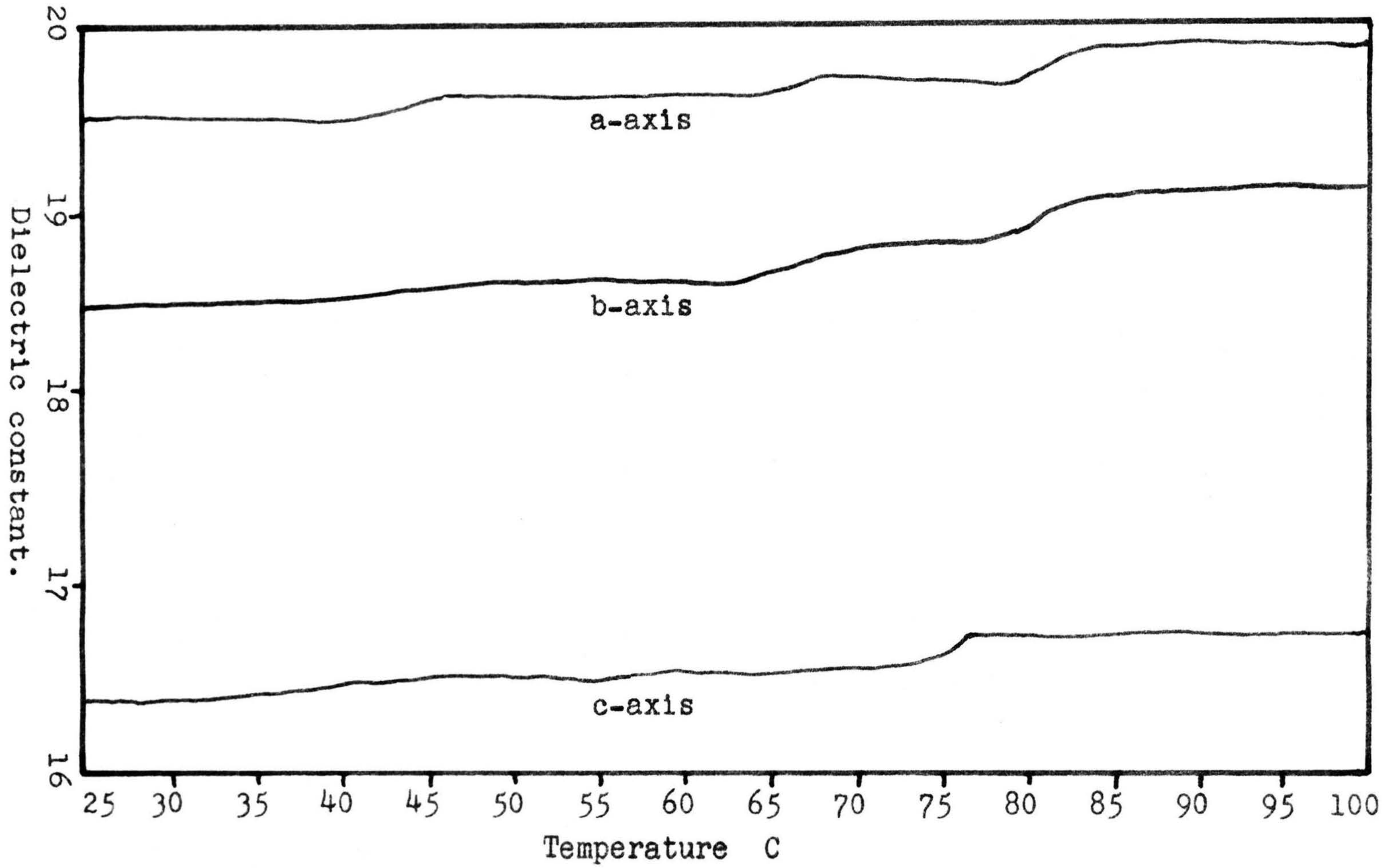


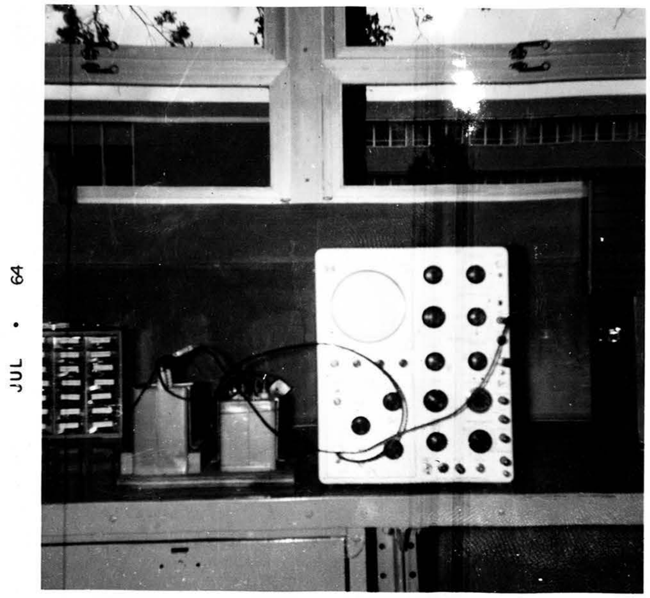
Figure 8. Dielectric constant of thallous nitrate vs. temperature along the a, b, and c, axis.

tion point (76 C.).

The characteristic hysteresis loop observable in ferroelectrics was searched for by placing the crystal in series with a much larger capacitor and applying an alternating voltage to the combination. The voltage across the sample was applied to the vertical plates of an oscilloscope and a portion of the voltage across the larger capacitor representing the charge was sent to the horizontal plates of the scope. For a picture of equipment and circuit drawing, see Figure 9. The dielectric hysteresis loop characteristic of ferroelectrics was not observed.

E. Piezoelectric Measurements

The main reason for examining the possible piezoelectric properties of the room temperature phase of thallium nitrate was to determine the exact space group of the substance (see discussion on page 18). The latest structural studies confirmed that the space group is Pbnm or Pbn2 (3). For an illustration of the structure of thallous nitrate based on Pbnm and Pbn2, see Figures 10 and 11. The space group Pbnm belongs to the point group mmm and the space group Pbn2 belongs to the point group mm2, both in the orthorhombic system. The point group mmm does not have piezoelectric properties. The piezoelectric matrix of point group mm2 is as follows (2).



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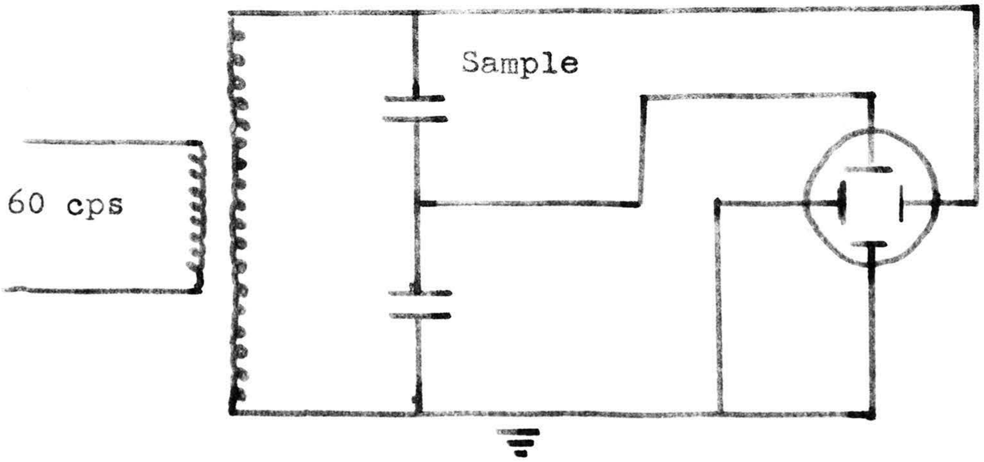

Figure 9. Circuit diagram and photograph of equipment used for dielectric hysteresis loop observation.

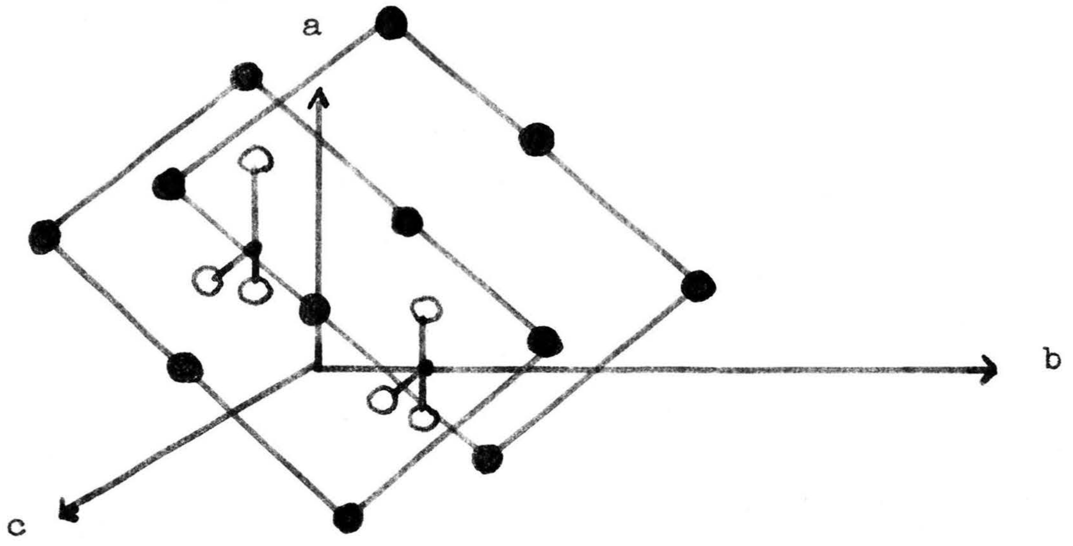

Figure 10. Structure of thallous nitrate based on Pbnm. Large dark circles represent thallium, light circles oxygen and small dark circles nitrogen.

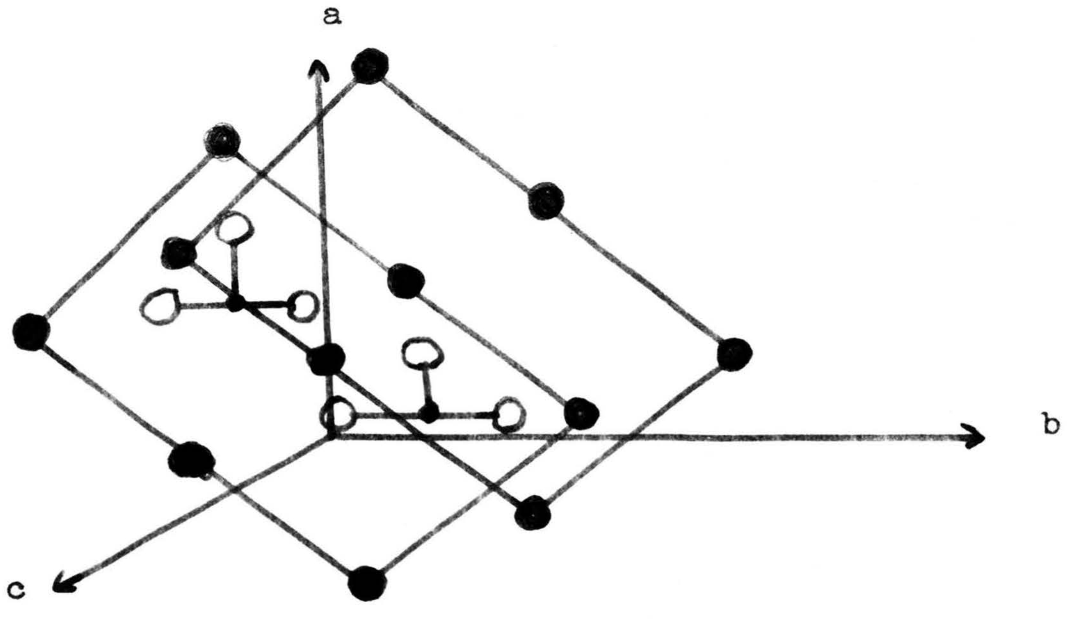

Figure 11. Structure of thallous nitrate based on Pbn2. A more symmetrical arrangement of oxygen around thallium would be found in this structure.

$$\begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & 0 & 0 \\ d_{31} & d_{32} & d_{33} & 0 & 0 & 0 \end{pmatrix}$$

With the knowledge of the allowable piezoelectric constants described by the class mm2 and the known orientations of the samples, if the substance has detectable piezoelectric properties, one can specify that the point group is definitely mm2.

The first method of piezoelectric investigation involved measuring the capacitance of a crystal as a function of frequency. For the data, see Table 4. The frequency range was from 1 kilocycle to 1 megacycle. For a picture of the equipment used, see Figure 12. In general a non-piezoelectric dielectric is represented by an equivalent electrical circuit of a capacitor in parallel with a resistor. A piezoelectric crystal has an equivalent electrical circuit of an inductor, resistor and capacitor in series, all of which are parallel with another capacitor. For a diagram of the equivalent circuit of a piezoelectric, see Figure 15.

In the case of a piezoelectric sample one would observe a significant change in capacitance in a fre-

TABLE 4

Capacitance vs. frequency data for thallous nitrate.

Frequency kc	C mmf
1	2.480
2	2.440
3	2.420
10	2.348
20	2.330
50	2.328
100	2.326
150	2.324
200	2.324
250	2.322
300	2.320
320	2.326
340	2.322
360	2.326
380	2.324
400	2.316
420	2.318
440	2.318
460	2.318
480	2.324
500	2.320
520	2.324
540	2.314
560	2.316
580	2.314
600	2.310
700	2.314
800	2.314
1000	2.318

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Figure 12. Capacitance Bridge used for piezoelectric measurements.

quency range near the mechanical resonant frequency of the crystal, while in the case of the non-piezoelectric this change is absent. For a graph of measured capacitance versus frequency data, see Figure 13. It is seen that the no significant change in capacitance of the crystal resulted from applying a variable frequency from ten kilocycles to one megacycle.

The second method of detection involved cutting three bars from a sample and electroding each bar in such a manner as to enable application of an electric field along the a, b, and c axes. The bars were placed in series with a 1000 ohm resistor, a variable frequency was applied to the circuit, and a voltmeter was placed in parallel with the resistor so that any peak voltage reading would indicate the presence of resonance. For a diagram of the circuit used, see Figure 14. Using this method no resonant frequencies were observed. All tests for piezoelectricity were therefore negative.

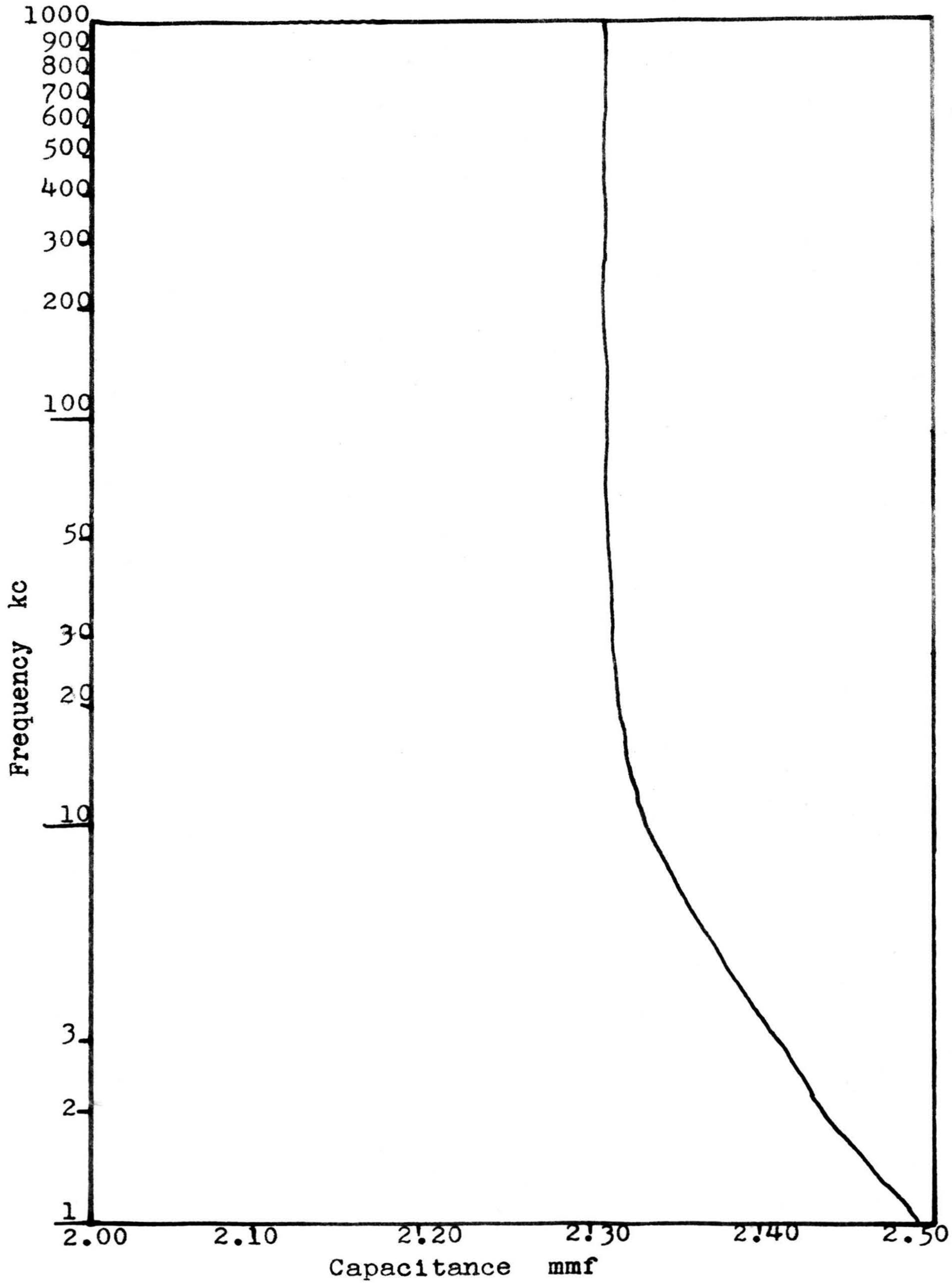

Figure 13. Capacitance vs. frequency for thallous nitrate.

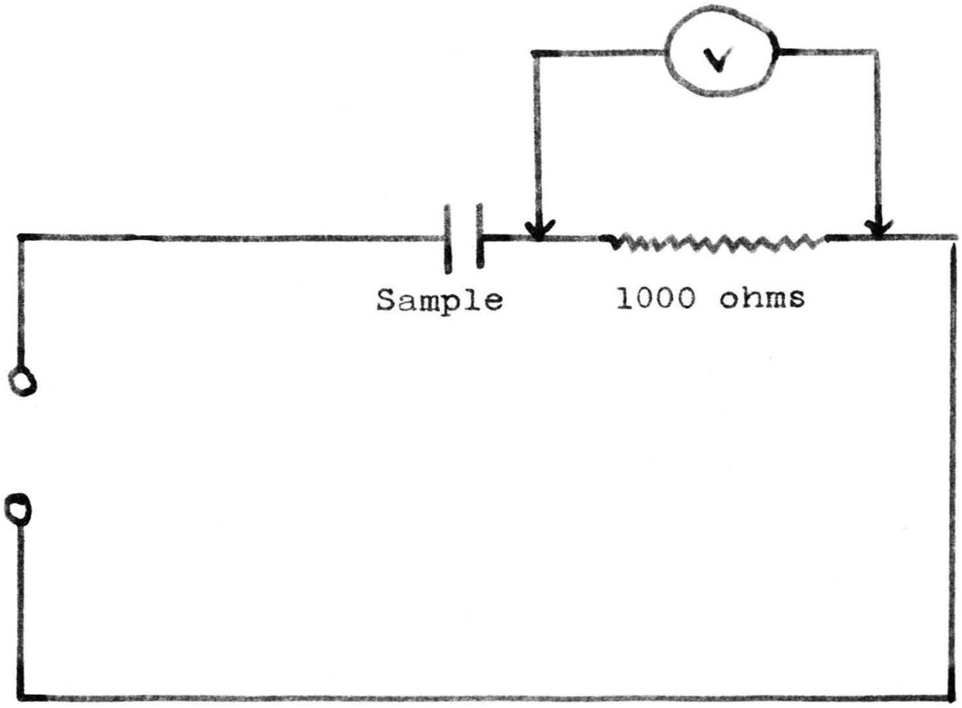

Figure 14. Circuit used for resonant frequency measurements.

DISCUSSION OF RESULTS

A striking feature of a ferroelectric is a high dielectric constant parallel to one or more of the axes, when measured near the Curie point. In general the dielectric constant of a ferroelectric shows that it has a behavior corresponding to the Curie-Weiss law for ferromagnetics. The Curie-Weiss law is

$$K = \frac{C}{T-T_c} \tag{9}$$

Where C = constant with dimensions of temperature,

T = variable temperature,

T_c= a constant representing a temperature close to the Curie point,

K = dielectric constant.

From the Curie- Weiss law it is readily seen that the dielectric constant of a ferroelectric becomes discontinous when the applied temperature reaches the transition temperature. It is also obvious that when the sample is heated to a temperature greater than the transition point the dielectric constant decreases rapidly as the temperature is raised. The first transition point above room temperature of thallous nitrate is 76° C. The compiled data in Table 3 and Figure 7 show only a slight increase in dielectric constant at the transition point, and there is no decrease in dielectric constant at temperatures greater than the transition point. The data indicates that thallous nitrate does not obey the Curie-Weiss law and therefore the room temperature phase is not a ferroelectric.

Latest structural studies indicate that thallous nitrate belongs to the space group Pbnm or Pbn2. To find the point group from the space group, the lattice symbol P, A, B, C, F, I or R must be dropped, all glide planes a, b, c, d, or n must be replaced by mirror planes m, and the subscript dropped from all screw axes. Using the rule mentioned above, the space group Pbnm corresponds to the orthorhombic crystal class mmm, and the space group Pbn2 is placed in the orthorhombic crystal class mm2. The orthorhombic crystal class mm2 is non-centrosymmetrical and therefore may be piezoelectric (25).

In an attempt to determine the exact space group of thallous nitrate. a crystal was placed in a capacitance bridge and the capacitance of the crystal was measured in a frequency range from one kilocycle to one megacycle. If the crystal of thallous nitrate was a piezoelectric, it would exhibit the same electrical properties as the equivalent electrical circuit shown in Figure 15 (26).

In Figure 15 the symbol L_1 represents the inductance due to the inertia of the motion of molecules in a piezoelectric. The symbol R_1 is the effective resistance and

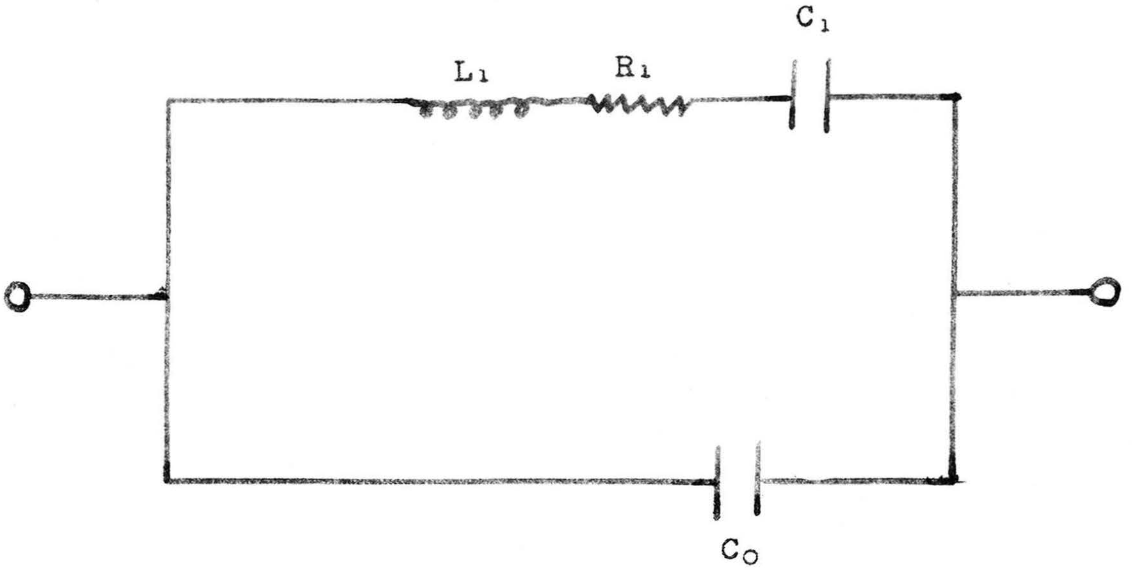

Figure 15. Equivalent circuit of a piezoelectric.

accounts for dissipation of electrical energy within the crystal. The letter C_1, represents that part of the free capacitance of the crystal which is added to C_0 when the crystal is free to expand and contract. The symbol C_0 denotes the so called clamped capacitance of a piezoelectric crystal, which represents the capacitance of the crystal when it is not able to change its dimensions.

With the knowledge of the equivalent electrical circuit of a piezoelectric circuit, it is evident that if thallous nitrate were a piezoelectric then a low frequency signal applied to the crystal would allow one to measure the free capacitance. It is also obvious that if a high frequency signal were applied to the crystal, the molecules in the crystal could not follow the rapidly changing field and only the clamped capacitance would be measured. So if thallous nitrate were a piezoelectric a change in frequency in the applied field from one kilocycle to one megacycle, would be accompained by a change in the measured capacitance of the crystal.

The data listed in Table 4 and plotted in Figure 13 illustrates no appreciable change in the crystal's capacitance with frequency. The crystal is at best a very weak piezoelectric, with about one third the piezoelectric activity of quartz. A search for resonant frequencies using the circuit described in Figure 14 verified the results of the capacitance versus frequency analysis, since again no piezoelectric properties were detected. If the crystal is piezoelectric at all, the resonances were suppressed by strong mechanical friction in the crystal. The result of this investigation is that no piezoelectric effect is detectable in thallous nitrate. The fact that no piezoelectric activity could be detected indicates that thallous nitrate belongs to space group Pbnm, although this classification is not definitely established.

CONCLUSIONS

The dielectric constants of thallous nitrate were measured as a function of frequency and orientation. No indication of ferroelectricity was found at the 76° C. transition temperature. Thallous nitrate does not exhibit a dielectric hysteresis loop. It is concluded that the 76° C. transition involves no ferroelectric phases.

The small variation of capacitance of a single crystal over the frequency range measured from one kilocycle to one megacycle, and the absence of piezoelectric resonances in the same range indicate that thallous nitrate is not detectably piezoelectric.

The result of this work favors classifying thallous nitrate in the centrosymmetric space group Pbnm.

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