RB-124

FERROELECTRICITY - PROPERTIES OF THIOUREA

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This bulletin contains a survey of the techniques employed in studying the electrical properties of ferroelectric substances. The material is presented in the form of an illustrative example dealing with the behavior of a new ferroelectric, thiourea[1]. An appendix describes in detail the apparatus employed for taking measurements. Thiourea was chosen for this purpose because in addition to displaying behavior characteristic of all ferroelectrics, it has a number of unique properties. These properties are of interest from both the point of view of physics in understanding the basic processes involved in ferroelectricity, and from the point of view of the application of ferroelectrics for fast memory devices, switches and other non-linear devices.

Introduction

The term *ferroelectric* is employed to describe a group of solids which exhibit a relationship between electric polarization, P, and applied electric field, E, which is analogous to that of the hysteresis loop observed in ferromagnetic materials. Further, there is a temperature, called the *Curie temperature*, T_c, above which this relationship disappears. In this temperature range, about the Curie temperature, the materials are said to be in the paraelectric state and may behave as linear dielectrics or may exhibit non-linearity and other anomalies in their physical properties.

The material employed in this study as an illustrative example is thiourea ($(NH_2)_2CS$), a common organic compound used extensively in the cosmetic, pharmaceutical and chemical industries as an intermediate in preparing various commercial products.

Preparation of Thiourea Crystals

For purposes of this study, it is necessary to prepare single crystals of thiourea large enough to be cleaved into thin plates. Since this compound is not stable at temperatures approaching its melting point, it was necessary to grow the crystals from solution. Methanol rather than water was employed as the solvent because crystals obtained from the latter were highly imperfect and contained large amounts of occluded solvent. Large crystals[2] were grown from the methanol solution by slow evaporation of the solvent at constant temperature.

A saturated solution of thiourea in methanol was placed in a cylindrical vessel which in turn was immersed in a water bath held at 30 degrees C by a mercury thermoregulator. Seed crystals were mounted on a glass "tree" which was rotated at 12 rpm. Since it was found that depleted solution which trails the growing crystals under conditions of unidirectional rotation causes clouding, the direction of rotation of the tree was automatically reversed every two minutes. The vessel containing the solution was fitted with a glass lid through which passed the thermometer and the stirring rod. Leakage around the lid openings was relied upon to provide a solvent evaporation rate of about 25 milliliters per week. The liquid level was maintained essentially constant over the growing period by occasionally adding thiourea in methanol saturated at 30 degrees C. The process was permitted to continue for about three months. For details of the temperature controlling circuit, see Appendix I.

Although the largest crystals were grown from seeds, there was appreciable excess nucleation on the "tree" and on the walls and bottom of the container. This proved to be a source of the more nearly perfect, though smaller, samples. The resulting crystals are completely colorless and, in many cases, perfectly transparent. Judging from the appearance and odor of the methanol solution at the end of the growth period, however, it is conceivable that the product is contaminated to some degree with impurities resulting from chemical attack of the methanol by thiourea.

Thiourea forms an orthorhombic Van der Waals crystal [space group, V^{16}_h (Pbnm)-centrosymmetric] with four molecules per unit cell according to room temperature data published by Wyckoff[3]. It is a very soft material having a distinct cleavage perpendicular to

the crystallographic [010] axis (referring to the orthorhombic axes as $c>b>a$). Since the ferroelectric direction is along the b axis, suitable samples are obtained by cleavage.

Electrodes are applied to the freshly cleaved surfaces. The method of electrode application and the electrode material presented some problems. In general, ferroelectric materials are electroded either by painting suitable conducting material or by evaporating a metallic film onto the surfaces of the crystal. It is essential to employ techniques and materials which result in low-impedance electrodes which adhere to the surfaces and which remain in place under the influence of appreciable changes in crystal dimensions accompanying the solid-solid phase transitions and piezoelectric strains. These requirements imply that the electrode material be a good conductor itself and not react chemically with the substrate. Conducting silver paint did not prove satisfactory for thiourea because of a reaction with the solvent-binder. Considerable difficulty was also encountered with evaporated silver or gold. First it was observed that, in the presence of atmospheric moisture, thiourea or its decomposition products react rapidly with these metals forming what appears to be metallic sulfides. Second, heating of the crystals by radiation from the evaporator causes sublimation and decomposition which, in turn destroys the continuity and adherence of the film. Third, on nearly every occasion in which metal film electrodes were successfully applied, the contact was destroyed after a few passes through the Curie temperature, either by wearing through of the film or by splitting or peeling of the metallic layer.

The currently most satisfactory electroding technique employs colloidal graphite ("Aquadag"). This forms what appears, on microscopic examination, to be an extremely intimate contact between the graphite and the thiourea. Evidently the combination of water solubility and the non-ionic nature of thiourea permits the solvent to clean the surface without causing flocculation of the graphite. This method of electroding has resulted in a perfect "yield" of "good" crystals as far as low-frequency hysteresis is concerned and no deterioration of the electrode has been observed over several weeks. It is conceivable, however, that graphite electrodes are not satisfactory at high frequencies (megacycle range) and hence a complete evaluation awaits measurements at these frequencies. Some success has also been achieved with gallium electrodes applied as molten gallium.

Low Field Dielectric Properties

As in the case of magnetic susceptibility in ferromagnetic materials, ferroelectrics exhibit an anomaly in the dielectric constant-temperature relation in the vicinity of a transition. The temperature dependence generally obeys a Curie-Weiss type of relationship:

$$\epsilon' = \epsilon'_o + \frac{const.}{T - T_o} \qquad (1)$$

Where ϵ' is the dielectric constant of the material, ϵ'_o is

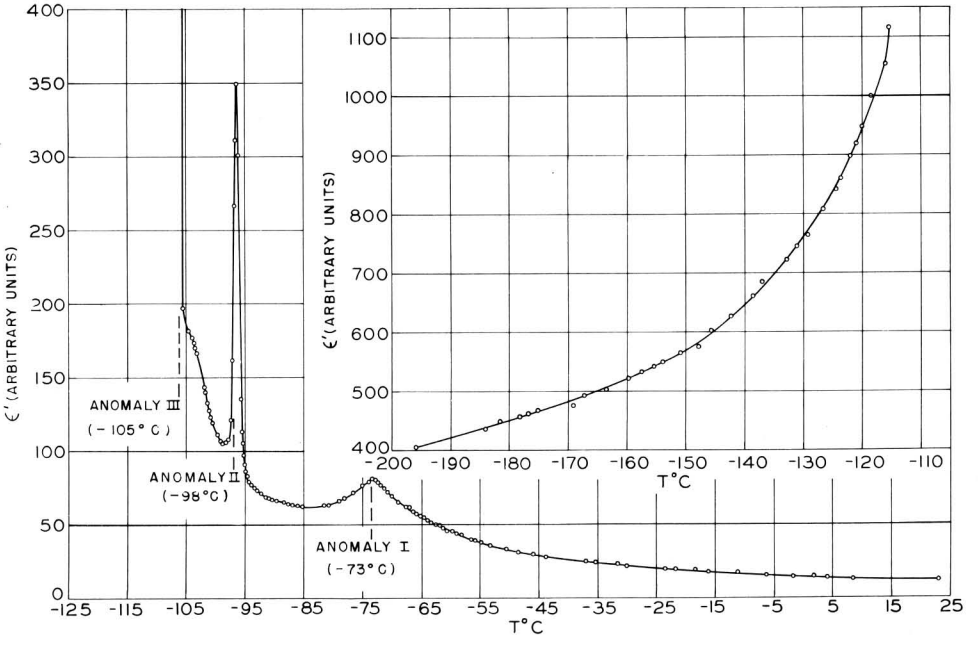


Fig. 1 – Temperature dependence of the dielectric constant in thiourea.

the residual dielectric constant, T is the absolute temperature in degrees Kelvin, and T_o is a characteristic temperature at which the dielectric constant approaches infinity. At the transition temperature, either a discontinuity or a maximum is observed in the dielectric constant depending on whether the transition is first or second order. In some materials, barium titanate, for example, the low field dielectric constant exhibits additional anomalies in the ferroelectric range corresponding to additional phase changes[4]. Emphasis is placed, in these considerations, on dielectric behavior at fields of magnitude much less than is required to produce domain-wall motion. Behavior at high fields is considered in the next section.

The temperature dependence of the dielectric constant in thiourea is shown in Fig. 1. The measurements were made on a conventional impedance bridge operating at 1000 cycles with a peak applied voltage of between 25 and 300 millivolts. (See Appendix II for details of the apparatus employed).

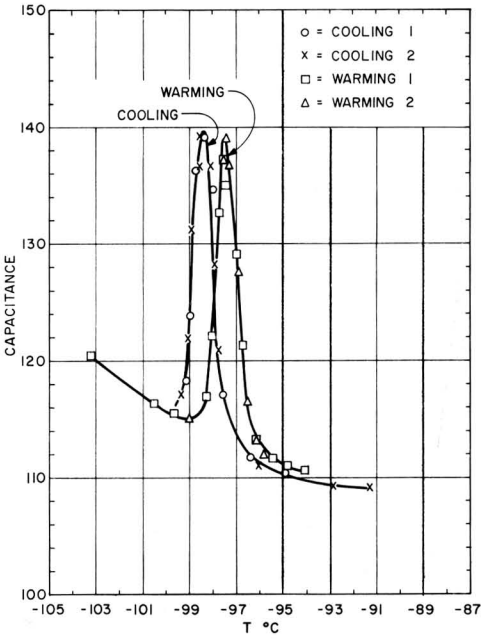


Fig. 2 – Thermal hysteresis of thiourea in anomaly II.

The relationship between the dielectric constant and temperature displays three anomalies over the temperature range considered. In order of decreasing temperature, the first (anomaly I) occurs at minus 73 degrees C, the second (anomaly II) at about minus 97 degrees C, and the third, (anomaly III) at about minus 105 degrees C. The third anomaly displays a distinct discontinuity, while the others obey a smooth temperature dependence. The point at which the discontinuity occurs is dependent upon a number of factors, and is not exactly reproducible from run to run. These factors include the rate at which the sample temperature is changed, the direction of the temperature change, the condition of the crystal with regard to external and internal stresses, and the condition of the electrodes. The second peak is characterized by having a half width of less than 1 degree C and peak-to-valley ratio of nearly four. It displays thermal hysteresis of about 1 degree C as shown in Fig. 2. The first anomaly shows a peak of smaller amplitude and greater breadth than the second. There is an observable thermal hysteresis associated with it. The value of the dielectric constant at room temperature is about 100.

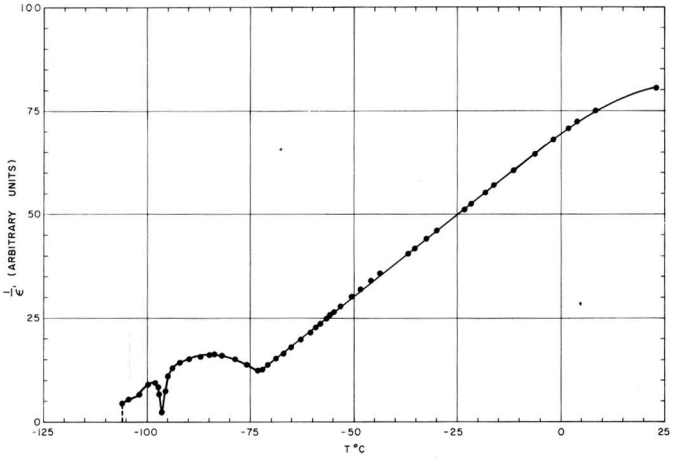


Fig. 3 – Temperature dependence of the reciprocal dielectric constant in the temperature range above anomaly III.

A plot of the reciprocal dielectric constant with respect to temperature from room temperature to minus 106 degrees C is shown in Fig. 3. Over a considerable range in temperature above the first anomaly, a reasonable correspondence to the Curie-Weiss law obtains. There is significant deviation near room temperature, and over the entire range there is evidence of slight curvature. This probably occurs because the ϵ'_o term in the Curie-Weiss relationship has not been taken into account. The straight line portion extrapolates to roughly minus 90 degrees C. In the region between minus 73 degrees C and minus 106 degrees C the behavior of the reciprocal dielectric constant is considerably more complicated and no simple relationship applies.

At temperatures corresponding to the region of the discontinuity and immediately below (between about minus 115 degrees and minus 105 degrees C) the dielectric constant becomes difficult to measure. This is apparently due to three factors: (a) the ϵ' vs. T relationship has so large a slope that reliable points can be obtained only in the absence of thermal gradients in the sample and with essentially perfect temperature regulation (neither of these conditions is met in the present experiment); (b) the ferroelectric coercive field is so low

in this temperature range that even at the lowest practical operating voltage of the bridge, it is not possible to avoid domain wall motion; (c) at least over part of this range there is a genuine discontinuity in the dielectric constant.

At temperatures below about minus 115 degrees C, however, the relationships are once more well-behaved and reproducible. A plot of the dielectric constant against temperature in this range is shown at the right in Fig. 1. There is no indication that a Curie-Weiss type of depedence is obeyed below the third transition as shown in Fig. 4.

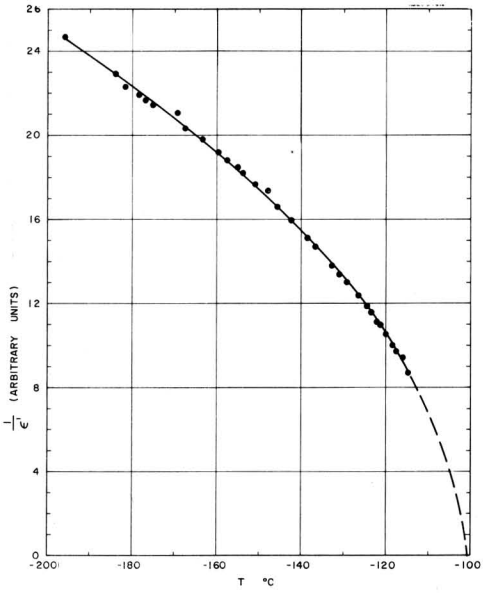


Fig. 4 – Temperature dependence of the reciprocal dielectric constant in the temperature range below anomaly III.

In addition to the point-by-point measurement of the dependence of the dielectric constant on temperature, this relationship was also studied employing a technique in which a quantity approximately proportional to ϵ' was plotted continuously against temperature. This technique makes it possible to detect irregularities in the ϵ'(T) relationship which could be overlooked in the point-by-point plot. Further, (see Appendix III) a simultaneous examination of the E vs. P dependence could be performed, permitting the detection of non-linearities in this relationship and correlating them with the dielectric anomalies.

The curve over the temperature range between room temperature and that of anomaly III, resulting from this prodecure is shown in Fig. 5. At very low fields, the results are essentially identical with those observed employing the point-by-point technique. A discussion of the behavior at higher fields and the corresponding P_{max} vs. E relationships is more appropriately taken up in the section which follows.

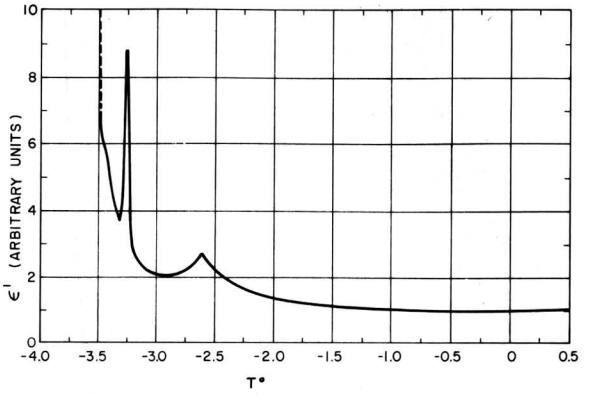


Fig. 5 – Temperature dependence of thiourea by the continuous plotting method.

For purposes of comparison there is shown in Fig. 6 a plot of the dielectric constant of Colemanite against temperature. This material is an example of a well-behaved ferroelectric in which there are no complications in the vicinity of the transition, and in which there is but one anomaly having a well-defined maximum.

Preliminary measurements have been carried out along the [001] direction. It is found that the dielectric constant is very low and appears to remain unchanged over the temperature range from room temperature to that of liquid nitrogen.

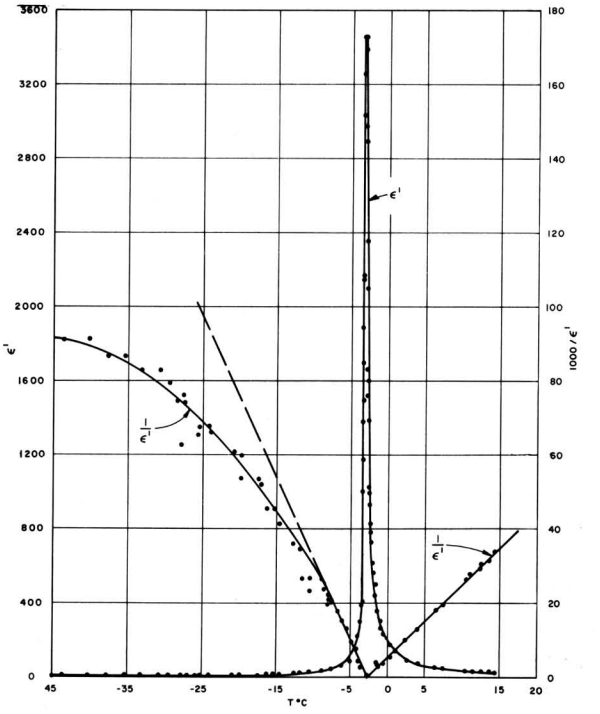


Fig. 6 – Temperature dependence of the dielectric constant and reciprocal dielectric constant in colemanite.

High Field Dielectric Properties

In the paraelectric state at applied fields up to breakdown or to dielectric saturation, whichever occurs first, one does not, in general, expect the dielectric properties of an insulator to be different from those observed at low fields. In a ferroelectric or anti-ferroelectric state, however, the high field region is defined as that range in which the dielectric susceptibility is a function of the applied field. In the ferroelectric case, these non-linearities exhibit ferroelectric hysteresis. In anti-ferroelectric materials, when non-linear behavior is observed, it is interpreted to result from the small energetic difference between the ferroelectric and anti-ferroelectric states which is manifested by a transition to the ferroelectric condition at appropriate field intensities. Thus, information regarding the state of a crystal as well as its behavior in that state is obtained from a study of the material at high fields.

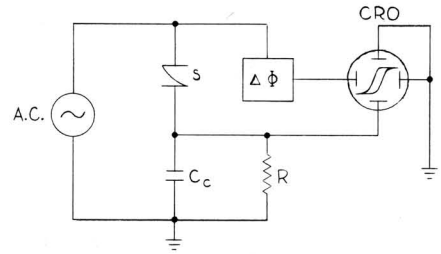


Fig. 7 – Sawyer-Tower loop tracer.

Complete characterization of a ferroelectric material includes, in addition to observation of the behavior at low fields in both the paraelectric and ferroelectric range, a study of the spontaneous polarization, coercive field, and switching time, all of which are observed at high fields. The first two measurements are made directly from the dimensions of the hysteresis loop, and the third, by observing the current pulse accompanying the application of a rectangular voltage pulse to the crystal.

The ferroelectric hysteresis loop is observed through the use of the Sawyer-Tower [5] circuit illustrated schematically in Fig. 7 (for details see Appendix IV). In brief, the technique provides a means whereby the charge Q stored in the ferroelectric capacitor may be displayed on an oscilloscope as a function of the applied voltage (V). The spontaneous polarization, P_s, is obtained by measuring the magnitude of the stored charge Q, at zero applied voltages. This may be expressed in terms of the comparison capacitor, C_c, and the dimensions of the sample:

$$P_s = VC_c/A$$

where V is the amplitude of the vertical deflection (see Fig. 8) on the oscillograph at zero field, and A is the electrode area. The coercive field, E_c is obtained from the thickness of the sample and the magnitude of the applied voltage at the point where the hysteresis loop crosses the $Q = O$ axis.

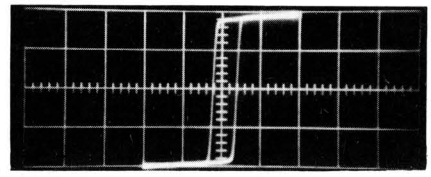


Fig. 8 – Ferroelectric hysteresis in thiourea (at 100 cps, 750 volts/cm peak).

From measurement of these quantities as functions of field, frequency and temperature, it is possible to characterize a given material relative to other known ferroelectrics, and to obtain significant information regarding the physical phenomena involved in the ferroelectric process. It is convenient, in comparing the behavior of a new material with other known ferroelectrics to select barium titanate, the most thoroughly studied and understood compound, as a standard. The following quantities represent the best values for barium titanate.

E_c = 500 volts/cm (at 60 cps and at room temperature); P_s (at room temperature) = 26×10^{-6} coulombs/curie temperature, cm^2; $T_c = 393^0$K.

The transition is first order, and hence the polarization is not strongly temperature dependent except over the range of the dielectric anomalies. The coercive field does depend to a considerable extent on the maximum applied field, the temperature, and the frequency.

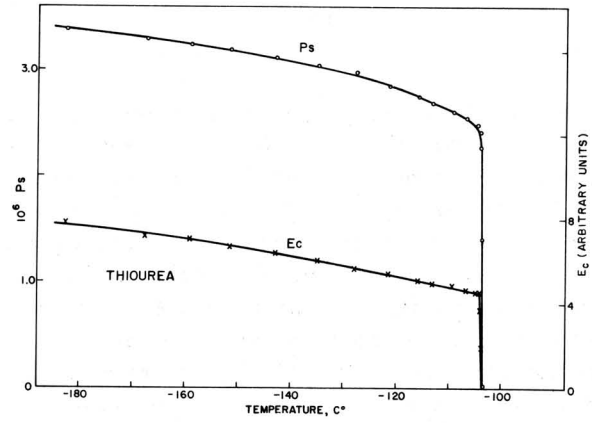


Fig. 9 – Spontaneous polarization, P_s, and coercive field, E_c, versus temperature in the range below anomaly III.

Present information on thiourea is largely qualitative, though the characteristic behavior is well estab-

lished. A plot of the spontaneous polarization and 60-cycle coercive field as a function of temperature in the range below anomaly III is shown in Fig. 9. The spontaneous polarization is of the order of 3 μ coulombs/cm^2 with coercive fields at temperatures well below the Curie point of the order of 200 volts/cm. The polarization behaves in the manner predicted for a first order transition (cf. e.g., Kittel, 1st ed., pp. 124-128) in that there is a pronounced discontinuity at the transition temperature. The coercive field follows the polarization rather closely except that near the transition, it appears to fall to zero before P_s reaches zero. As illustrated in Fig. 10, the hysteresis loop narrows to vanishingly small values as the temperature approaches that of the transition.

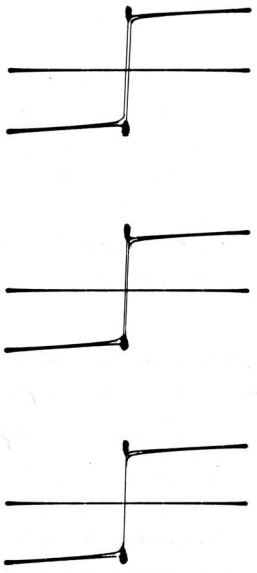


Fig. 10 – Hysteresis in thiourea near the Curie point.

Also characteristic of first order ferroelectric transitions is the behavior of the P vs. E relation as the temperature is raised to values above the Curie temperature, T_c. At the top of Fig. 11 is a set of hysteresis loops observed in the range above the Curie temperature. Here the crystals shows normal paraelectric behavior at relatively low fields, while at higher fields, it displays hysteresis. This is indicative of the dependence of the transition temperature on applied field. Even though the temperature is above T_c, as the field increases a point is reached at which the crystal suddenly becomes ferroelectric. The transition temperature is linearly dependent on the applied field as indicated in Fig. 11.

In this range, thiourea behaves essentially as one would predict for a ferroelectric material exhibiting a first order transition. The abrupt drop in the coercive

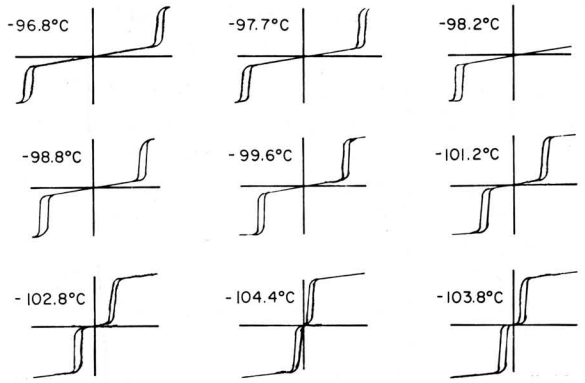
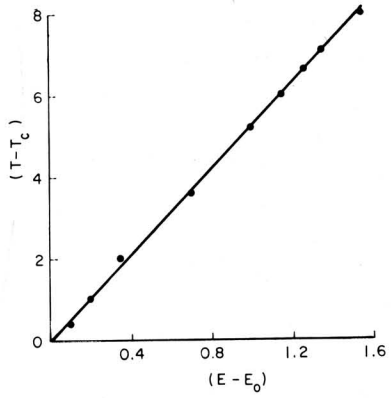


Fig. 11 – (a) Double hysteresis loops in thiourea.



(b) Field dependence of the Curie temperature in thiourea.

field which occurs at a temperature slightly lower than that of the discontinuity in the spontaneous polarization is the only aspect of its behavior which has not, to our knowledge, been found previously in other materials. In the range of temperatures immediately above this region, however, the behavior does not lend itself to so direct an interpretation. This is evident first from the appearance of two additional anomalies in the dielectric constant. By employing the method of continuous plotting of the dielectric constant and simultaneous observation of the P vs. E relationship on an oscillograph, the presence of a new ferroelectric phase was detected over the narrow temperature range of anomaly II. The hysteresis loop which identifies this as a ferroelectric state is illustrated in Fig. 12. It is characterized by having a spontaneous polarization of the order of 10^{-9} coulombs/cm^2 and a coercive field of the order of 1 volt/cm. It should be noted that in the presence of hysteretic behavior

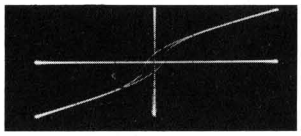


Fig. 12 – Hysteresis loop of thiourea in anomaly II.

with so low a coercive field, it is doubtful that the low field dielectric constant described in the previous section is truly "low field" over this temperature. No hysteresis is observed on either side of this region, nor are any non-linearities evident in the vicinity of anomaly I. Throughout the temperature range of anomaly II, the coercive field appears to remain essentially constant, while the spontaneous polarization displays the behavior indicated in Fig. 13. The polarization reaches a maximum at about the same temperature as that of the maximum in the dielectric constant and drops symmetrically to zero on either side of the anomaly. These observations are consistent with the conclusion that the minima in dielectric constant which occur at either side of anomaly II are associated with an upper and lower Curie point for this transition.

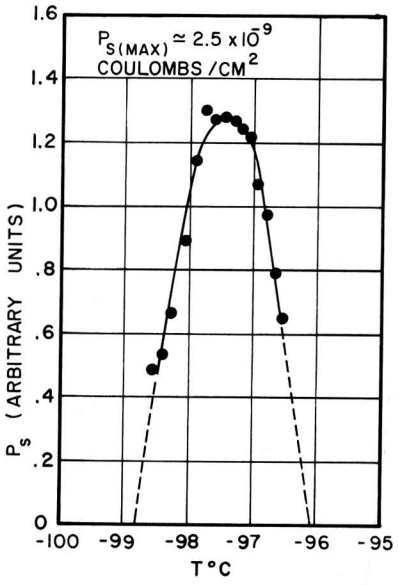


Fig. 13 – Temperature dependence of the spontaneous polarization of thiourea in anomaly II.

Switching Behavior

Information regarding the behavior of ferroelectric domains with respect to domain wall motion and the formation of new domains can be obtained from a study of the switching behavior of a ferroelectric capacitor. These investigations also lead to measurements of the rate at which information can be read into and out of a ferroelectric element. A detailed analysis of switching behavior in barium titanate reported by Merz [6], has formed the basis of a significant part of current thought concerning these processes in ferroelectrics in general.

The measurements are performed by applying to the sample sequences of voltage step functions (i.e., square

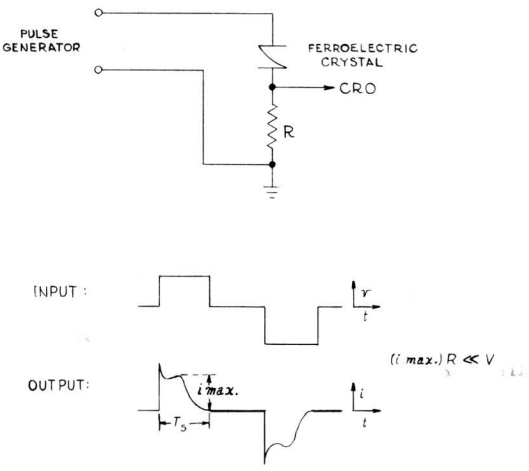


Fig. 14 – Measurement of switching time.

pulses of duration greater than that of the phenomenon under study), first of one polarity and then of the other and observing the current passing through the crystal as a function of time (Fig. 14). The switching current and switching time (i_{max} and t_s), as shown in Fig. 14, are observed as functions of applied field strength and of temperature. (See Appendix V for details of the pulse generator employed).

Although measurements of switching time are incomplete at this time, the following tentative conclusions have been reached:

(a) The switching time at temperatures not too far below that of the transition (Anomaly III) are of the order of 10^{-7}, seconds for moderate fields and thick samples. (Fig. 15).

(b) Thiourea is stable and well behaved under random switching and it has a "good memory".

(c) The relationship between field and switching time reported by Merz for barium titanate were not found to hold in the one sample investigated (Fig. 16).

(d) Thiourea, as in the case of other ferroelectrics, can be switched at what appears to be arbitrarily low fields.

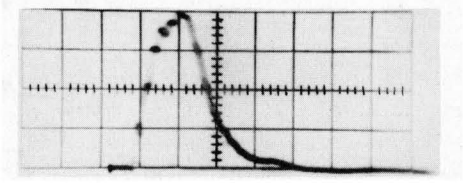


Fig. 15 – Switching curve – thiourea. E=4600 volts/cm, τ=0.2 microseconds per division, T = -107 degrees C.

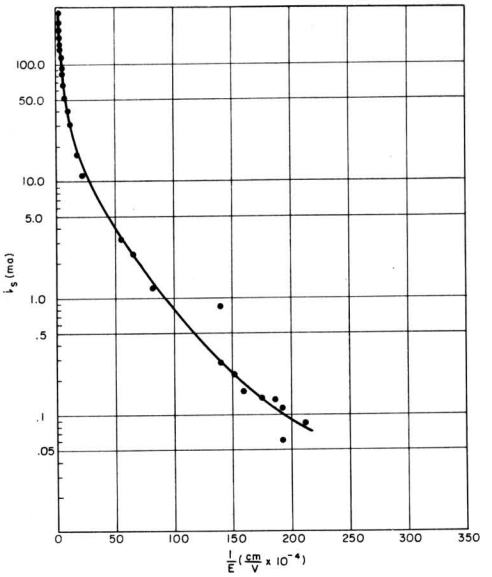


Fig. 16 – Thiourea switching current vs reciprocal field.

Summary and Conclusions

Over the temperature range between minus 106 degrees C and minus 70 degrees C the dielectric constant of thiourea displays three anomalies, two of which correspond to ferroelectric transitions. In the absence of structural data and of more complete electrical measurements, whatever conclusions reached regarding the origin of these anomalies are of necessity speculative. The good correspondence of the dielectric behavior to a Curie-Weiss type of relationship in the temperature range above that of anomaly I (above minus 73 degrees C) together with the absence of observable non-linearities in the P vs. E relationship points to the possibility that the anomaly I transition is to an anti-ferroelectric state. As the temperature is decreased, the crystal goes over to a ferroelectric state over the range of anomaly II and then to a state which is indeterminate. The shoulder in the ϵ' vs. T plot at temperatures immediately above that of anomaly III suggests the possibility of a third transition which occurs just prior to the first order ferroelectric transition.

This material shows switching which is faster than that of the best barium titanate crystals with moderate fields. It displays "good memory" as well and appears to be free of fatigue effects. The coercive field is relatively low.

As yet, there is insufficient information from which a theoretical model for ferroelectric behavior in this material could be constructed. One is tempted, in view of the composition of thiourea and in light of our understanding of ferroelectric behavior in other hydrogen containing compounds, to associate the ferroelectric behavior with ordering of hydrogen bonds. X-ray studies of the structure are under way and some thought is being given to the further investigation of the behavior of the hydrogens through infra-red absorption spectrometry and nuclear magnetic resonance. Studies of the switching properties and of the influence of the electrodes and the crystal surface on the electrical behavior are being continued. A third avenue of investigation being followed is the introduction of isotopic substitutions for the hydrogens and a study of substituted thioureas.

George J. Goldsmith

Appendix I

Control Circuit for Crystal Thermostat

Temperature control for the growing of ferroelectric crystals is achieved by means of a constant temperature water bath which surrounds the crystallization vessel. The temperature sensitive element is a glass capillary filled with mercury. The heater control circuit which has met all our requirements for reliability and stability over several months continuous operation is illustrated in Fig. I-1.

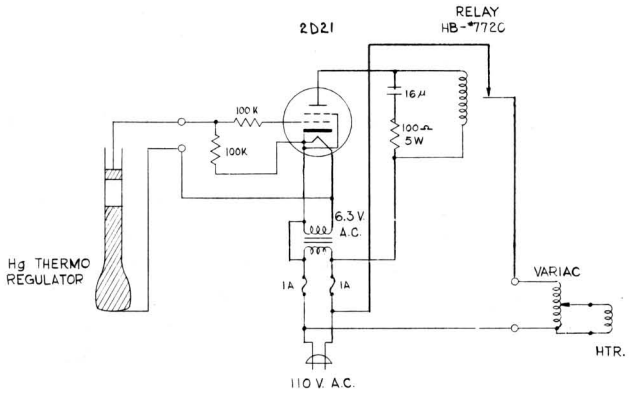


Fig. I-1 – Thermoregulator circuit for water bath.

Appendix II

Measurement of Dielectric Constant at Low Fields

The method employed for a measurement of the dielectric constant involves the construction of a capacitor the dielectric of which is the ferroelectric material under study. The capacitance is then measured with an impedance bridge. Since the low field dielectric constant of these materials is of importance, the bridge null detector must be designed to operate at extremely low signal levels. The case under consideration here requires that a null to within 0.1 $\mu\mu f$ be detectable at a total bridge voltage of 25 millivolts (rms).

The bridge itself is a commercial impedance bridge (ESI Model 250 C1) which is of the modified DeSauty type (R-C) when used for capacitance measurement. The bridge is

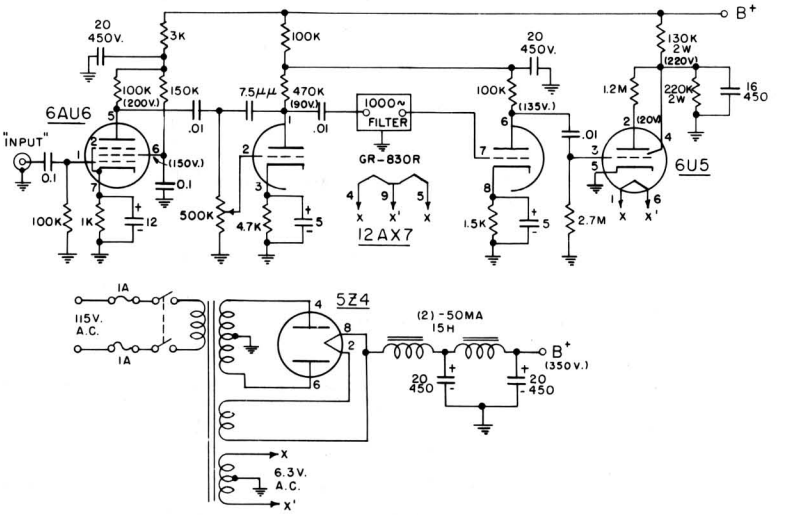


Fig. II-1 – Null indicator for 1000 cps.

powered by a Hewlett-Packard (Model 200 AB) signal generator at 1000 cycles. The null detector (Fig. II-1) consists of a tuned amplifier and a "electron eye" indicator. The tuning element is a General Radio 830 R 1000-cycle band-pass filter which has a bandwidth of about 10 cycles. The amplifier is tuned to improve the signal-to-noise ratio and to reject harmonics which may be generated by the crystal because of non-linearities in the capacitance.

Appendix III

Continuous Simultaneous Measurement of the ϵ' vs. T and the P, (E) Relationships

In surveying materials, it is frequently convenient to be able to perform a rapid determination of the temperature dependence of the dielectric constant. Many methods have been evolved whereby this can be accomplished through the use of servo-mechanisms operating an impedance bridge. In most cases, however, one is interested principally in a qualitative measure of this relationship. For this purpose the simple method illustrated in Fig. III-1 is suitable and offers the additional advantage of a simultaneous display of the P, (E) relationship.

In this method, the comparison capacitor, C_c is chosen to have a value which is very large compared with that of the ferroelectric capacitor, FE. Then the voltage seen across the comparison capacitor at constant applied voltage and frequency is proportional to the dielectric constant of the ferroelectric in the linear range and to B_{max}, the maximum displacement, in the non-linear regions.

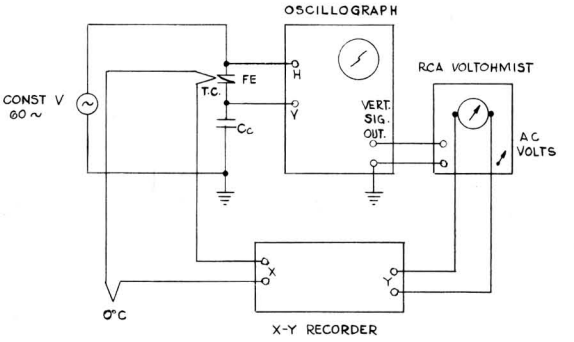


Fig. III-1 – Continuous recording of ϵ vs T.

Appendix IV

Ferroelectric Loop Tracer and Control Panel

In the precise measurement of the important parameters of a ferroelectric, (P_s, E_c, ϵ'), it is necessary to employ both a capacitance bridge and a loop tracer. In general, the quantities P_s, and E_c are obtained by photographing the ferroelectric hysteresis loop as displayed by an oscillograph and subsequently measuring the dimensions of the loop, while, as explained above, the dielectric constant is measured with an impedance bridge. Since these quantities are usually measured as a function of temperature it is convenient to be able to perform all the measurements quickly and without disturbing the sample or its leads. This latter point is particularly important in the capacitance measurement since the "zero" capacitance of the bridge plus its connecting wires is dependent somewhat on the physical position of the wires.

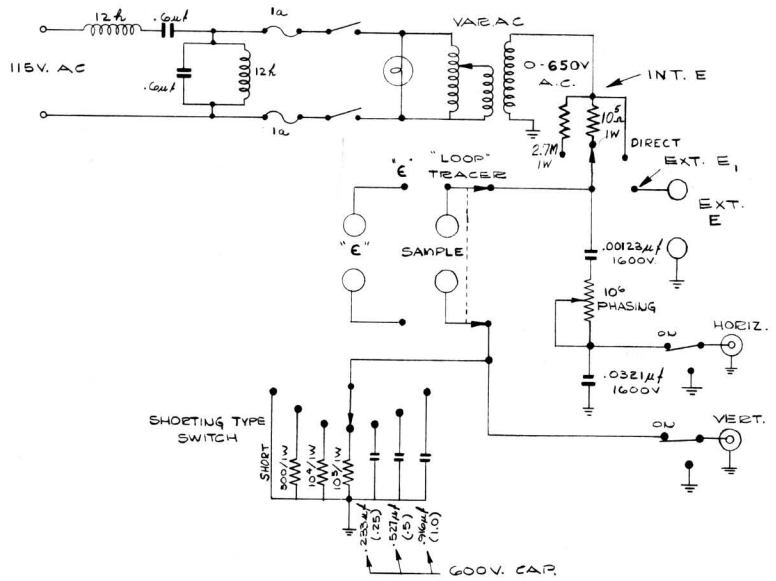


Fig. IV-1 – Control panel.

With these requirements in mind the control system illustrated in Figs. IV-1 and IV-2 was constructed. It provides for switching from the loop tracer to the impedance bridge at any time; observation of both the hysteresis loop and its derivative; measurement of losses; electrical display of the coordinate axes of the hysteresis loop and application of required voltages.

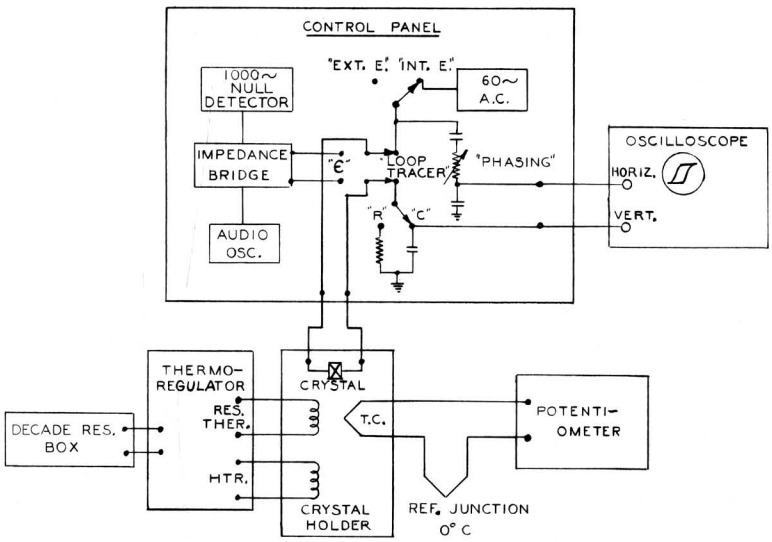


Fig. IV-2 – Functional block diagram for testing ferroelectric crystals.

Appendix V

Pulse Generator

The requirements for a pulse generator employed in switching time measurements are the following: (a) pulses of either polarity must be delivered to the same output; (b) they should be of variable amplitude and width over a wide range of voltage and time,

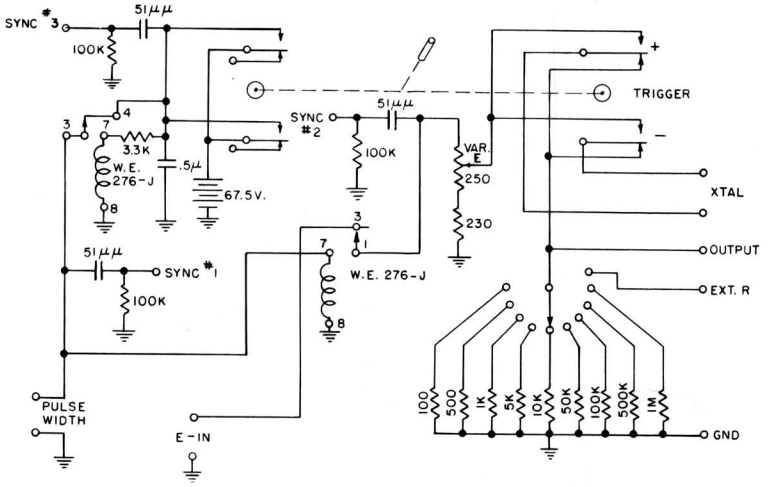


Fig. V-1 – Pulse generator.

and (c) the pulse source should be of very low impedance so that currents approaching one ampere may be drawn.

The pulse generator illustrated* in Fig. V-1 serves admirably for this purpose. The pulses are generated by a mercury relay which is driven from a second mercury relay which provides synchronization information. The voltage source may be batteries or any other power supply. The pulse width may be varied from a millisecond to minutes by connecting suitable capacitors to the "pulse width" terminals. The pulse rise time is of the order of 10^{-8} seconds.

Appendix VI

Control of Crystal Temperature

In the early measurements with thiourea, no attempt was made to control the temperature of the crystals. The sample holder was designed to have poor thermal communication with room temperature and was cooled by radiation and conduction to a liquid nitrogen heat sink. The rate of cooling was adjusted by varying the spacing between the heat sink and the sample holder. In general, this method was satisfactory for surveying and measuring the electrical properties over a wide temperature range. It had the disadvantage, however, of being very slow and not permitting convenient maintenance of an arbitrary temperature. When it became apparent that more precise temperature control was necessary, a complete system was designed and constructed.

The mechanical and electrical design of this system is shown in Figs. VI-1 and VI-2. During operation of the system, the sample is placed in contact with a silver block of large heat capacity. The silver block is isolated from room temperature by a thin-walled stainless steel support and is heated by an internal nichrome heater. Cooling is achieved by radiation and conduction to a surrounding brass cylinder which is immersed in liquid nitrogen and which is also isolated from the room by a similar stainless steel support. Conduction to the cold brass may be controlled by the introduction of an exchange gas into the space surrounding the silver block. In practice up to the present, this exchange gas has been air at one atmosphere at room temperature. Convection currents are minimized by Teflon baffles. The temperature of the silver cylinder is

*A modification of a similar pulse generator designed by J. R. Anderson, National Cash Register, private communication.

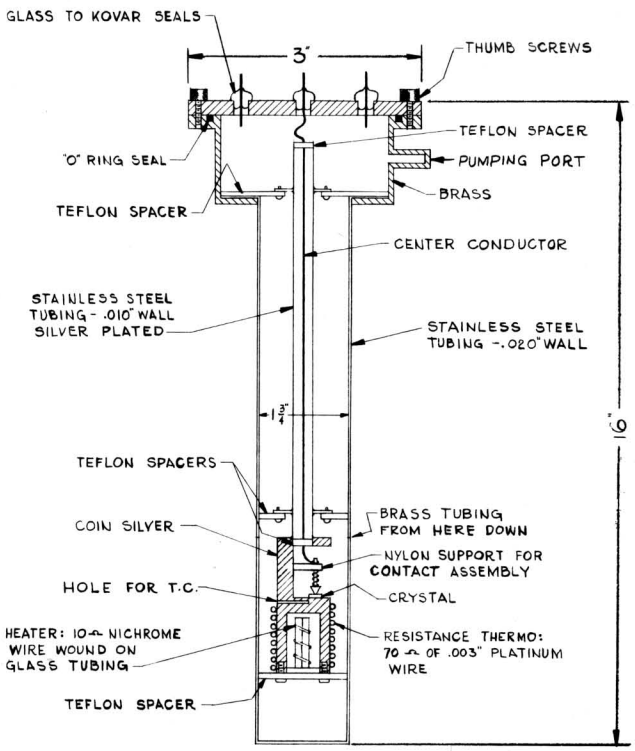


Fig. VI-1 – Cryostat.

sensed by a platinum resistance thermometer wound directly on it with a thin layer of Araldite as the electrical insulation. The sample temperature is measured by a copper-constantan thermocouple inserted in the silver immediately beneath the sample. Electrical connection to the sample is made by a thin wire passing coaxially through the inner stainless steel support to a spring-loaded plunger. The other contact to the sample is made through the silver block which is connected to a thin silver plating over the support rod. This system provides a low loss coaxial connector of low capacitance. The various leads are brought out through Kovar-glass vacuum seals at the top of the sample holder.

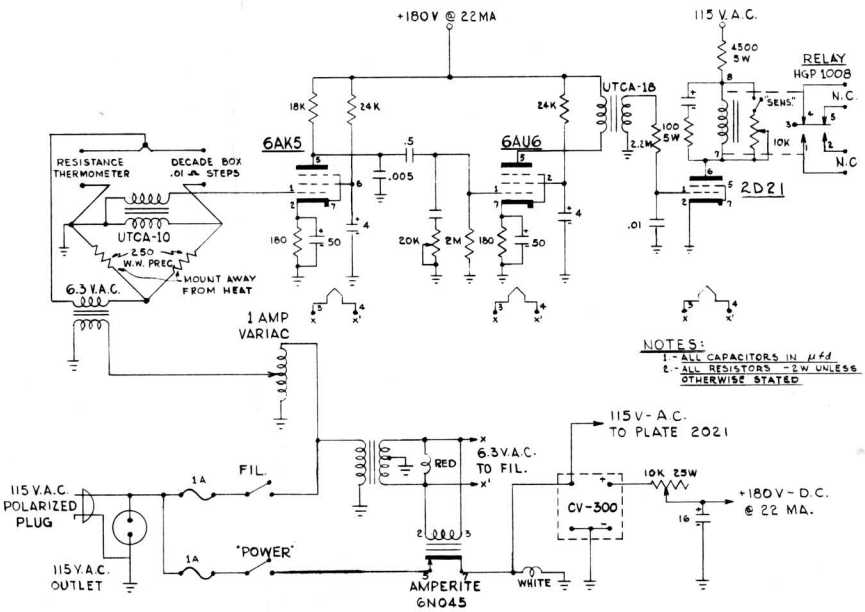


Fig. VI-2 – Thermoregulator for resistance bridge.

Temperature control is provided by making the resistance thermometer part of an a-c operated resistance bridge the other legs of which are a decade box of 0.01-ohm steps and two precision fixed resistors. The bridge signal is amplified and fed to a thyratron, the plate supply of which is the same a-c source which operates the bridge. This becomes, then, a phase-sensitive synchronous detector. The thyratron operates a sensitive mercury relay which interrupts the heater supply.

In operation the relay contacts are shunted by a resistance chosen to permit a steady current to flow which is 50 percent to 90 percent of the maximum heater current when the reply contacts are closed. This shunt current is selected to be nearly sufficient to maintain temperature in the desired range. For example at minus 100 degrees C, the shunt current is about 0.8 ampere and the total current about 1.1 amperes. Reliable control to within ± 0.05 degree C has been obtained from liquid nitrogen temperatures to room temperature.

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