Surface Space-Charge Layers in Barium Titanate

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Above the Curie temperature, pyroelectric currents can be produced in single crystals of barium titanate even though there is no electric field applied. The polarization that remains at these temperatures is ascribed to space-charge fields in the crystal. From studies of the wave forms of the pyroelectric current signals it is concluded, tentatively, that space-charge layers of up to 10^{-5} cm in thickness reside at the crystal surface and that these space charges also produce a field through the interior of the crystal. Further evidence for space-charge fields is provided by the occurrence of an associated photovoltaic effect and by asymmetrical hysteresis loops. The space-charge fields vary considerably in magnitude from crystal to crystal. In general, they can be modified by suitable heat treatment but return to their original condition when fields are applied above the Curie point.

The space charge fields apparently influence the direction in which the domains polarize when the crystal is cooled through the Curie point. They will also affect capacity measurements above the transition and will influence the actual temperature of the transition. It is quite possible that the fields play an important role in the process of domain nucleation.

INTRODUCTION

ON the basis of x-ray and electron diffraction experiments with very small particles of $BaTiO_3$, Känzig has suggested[1] that there exists an ionic or electronic space charge layer at the surface of the crystal. As he points out, this layer will not disappear simply by heating the crystal through the Curie point of the bulk crystal because the properties of the space-charge layer do not depend sensitively upon the temperature as long as the conditions for dielectric saturation are fulfilled. Consequently, the surface layers of the crystal will remain spontaneously polarized at temperatures above the Curie point. The x-ray and electron diffraction experiments[2] do indicate, in fact, that the surface layers remain tetragonal above the Curie point.

In the temperature range immediately above the Curie point, the polarizability of the crystal is very high and varies rapidly with the temperature. This suggests that above the Curie point, any spontaneous polarization in the space charge layer should give rise to an appreciable pyroelectric effect. The author has described elsewhere a dynamic method for studying the pyroelectric effect.[3] The crystal is subjected to brief intense flashes of light by means of a rotating chopper. During the flash the temperature of the crystal changes at the rate dT/dt and consequently, the spontaneous polarization changes at the rate dP/dt. This rate of change of the polarization is recorded as a current, i, in an external circuit, where i can be written

$$i = A\left(\frac{dP}{dt}\right) = A\left(\frac{dP}{dT}\right)\left(\frac{dT}{dt}\right), \qquad (1)$$

where A is the area of the crystal. It was shown for the dynamic technique that the factor dT/dt that occurs in

(1) is approximately independent of the actual temperature of the crystal if the specific heat at constant stress remains approximately constant. Then, as the conditions of the experiment are varied, any changes in the pyroelectric current, i, are reflecting to a first approximation, changes in the factor dP/dT, the pyroelectric coefficient. It has been shown also that dP/dT is still the dominant factor even close to the Curie point where the specific heat is fairly temperature dependent. The details concerning the mounting of the crystals and their electrodes have been fully described elsewhere.[3]

EXPERIMENTAL OBSERVATIONS

As will be discussed later, the light gave rise to a weak photovoltaic current simultaneously with the pyroelectric current. The experiments to be described were performed at temperatures above the Curie point and, because of their different features, it was possible to distinguish between the two components of the total current produced by the light. Figure 1 shows, schematically, the way in which the total current behaved during a long (i.e., several seconds) light pulse. Immediately on switching on the light a high pulse of current could be observed by using the oscilloscope. This current decayed with a time constant of the order of a millisecond to a value two or more orders of magnitude lower than its peak value. The subsequent behavior of the current was studied using a sensitive electrometer. The current following the initial high peak showed a further slow and slight decay, eventually reaching a steady value. On turning off the light there was an immediate transient current, approximately equal to the initial transient in magnitude and duration, but in the opposite direction. This brief, high current was then followed by a small current that decayed slowly to zero.

The small steady current is identified as the photovoltaic current while the much larger transient currents are pyroelectric in origin. It is theoretically possible for

[1] W. Känzig, Phys. Rev. **98**, 549 (1955).
[2] Anliker, Brugger, and Känzig, Helv. Phys. Acta **27**, 99 (1954).
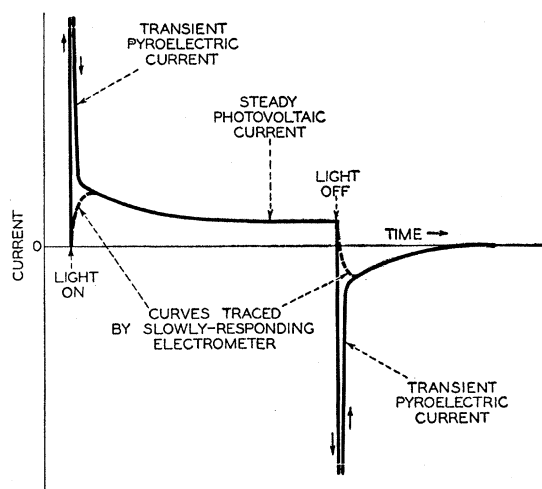[3] A. G. Chynoweth, J. Appl. Phys. **27**, 78 (1956).

FIG. 1. Schematic diagram showing the time variation of the current during a slow light-dark cycle. The pyroelectric and photovoltaic components of the total current are indicated.

a photovoltaic current to decay to zero if the carriers freed by the light become trapped so as to set up a space-charge field opposing the field originally present. However, one cannot explain by this mechanism the high transient current in the reverse direction and the return of the crystal to its initial condition simply by turning the light off. Strong evidence for the existence of the two current components was provided by experiments in which the spectral quality of the light was varied. When the tungsten light was filtered so as to allow only wavelengths longer than about 4400 A to reach the crystal, the steady current was two or more orders of magnitude smaller than the initial peak. Now the absorption edge of BaTiO$_3$ occurs at about 4100 A. Replacing the filter by one absorbing only those wavelengths shorter than 3800 A produced more than an order of magnitude increase in the photovoltaic current while there was only a very slight increase in the peak current. The large increase in the photovoltaic current is no doubt due to the liberation of carriers by the short-wavelength light but as the total radiated energy falling on the crystal does not increase very much when the filter is changed, the pyroelectric current likewise shows only a small increase. For all the experiments described in this paper, the light was filtered so as to allow only wavelengths longer than 6100 A to reach the crystal. Under these conditions it may be safely concluded that the high transient currents are pyroelectric in origin and that the current pulses observed when the crystal is subjected to chopped light have a completely negligible photovoltaic component.

To follow the pyroelectric current through the Curie point as determined by the spontaneous polarization, the crystal was first polarized by a static negative saturation field ($\sim$10 000 volt/cm) at room temperature, the field being removed for the experiment. The

crystal was then slowly warmed, measurements being taken of the height of the pyroelectric current pulses displayed on an oscilloscope. The behavior of the current as a function of temperature is shown in Fig. 2 where the current is plotted using two scales in order to make clear the readings above the Curie point. The rapid increase of the current as the Curie temperature is approached is readily explained by the steepening of the polarization-temperature curve. As the Curie point in barium titanate is a first-order transition, the spontaneous polarization should disappear completely in a discontinuous manner. A discontinuity will also appear in the slope dP/dT of the curve, while above the Curie point, if the spontaneous polarization is zero, the pyroelectric coefficient will be zero. Though the discontinuity is evident in Fig. 2, it is also clear that an appreciable pyroelectric coefficient, and hence a spontaneous polarization, persists to temperatures well above the Curie temperature. This residual polarization was observed in all the crystals studied though to varying extent.
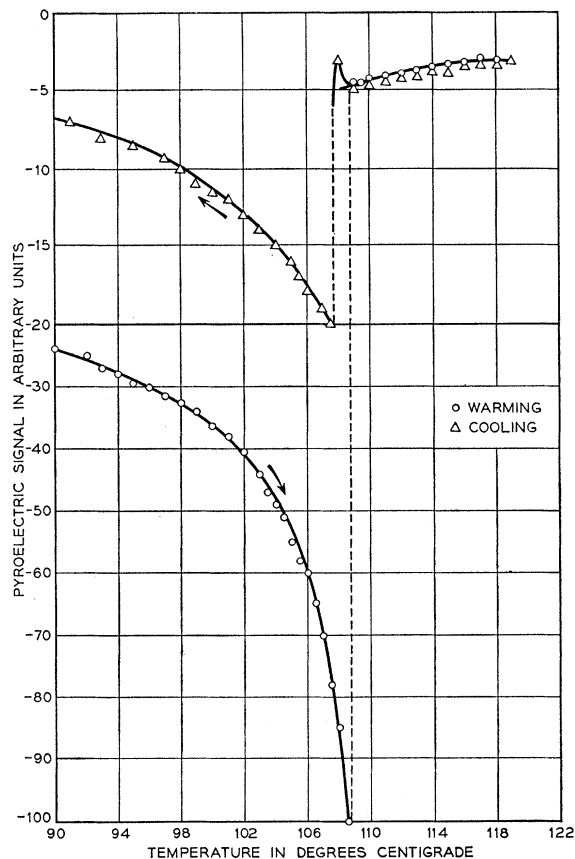

FIG. 2. The variation with temperature of the pyroelectric current due to the spontaneous polarization on raising and lowering the crystal through the Curie point, the crystal having been polarized previously at room temperature with a saturation negative field. Note the two scales used on the pyroelectric current axis.
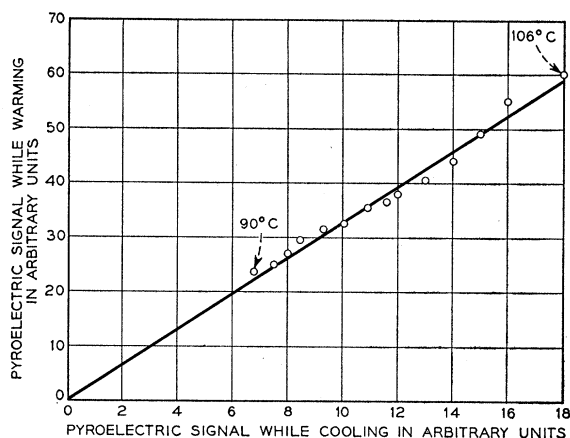
FIG. 3. The pyroelectric signal for the fully polarized crystal measured while raising the crystal temperature from 90°C to the Curie point plotted against the signals measured while cooling over the same temperature range, the crystal being only partly polarized while cooling.

Also shown in Fig. 2 is the pyroelectric signal measured while the crystal cooled slowly through the Curie point. Above the transition the cooling curve follows the points obtained while warming, to within experimental error. At the transition, the pyroelectric signal suddenly increases to an appreciable value and then falls off with the temperature in the same way as do the points on the "warming" curve. This correspondence is made more evident by the roughly linear plot of Fig. 3 where the pyroelectric signals obtained while warming and cooling are plotted against each other over the temperature range 90°C to the Curie point. Thus, the net spontaneous polarization of the crystal when the domains are partly oriented has the same dependence on the temperature as when it is fully oriented.

In Fig. 4 is shown the variation of the pyroelectric signal with temperature, both warming and cooling, after the crystal had been initially polarized at room temperature with a *positive* saturation field. Up to the Curie point, the warming curve behaves in the expected manner. At the Curie point, there is a sudden discontinuity and a residual pyroelectric signal appears but in the reverse direction. On further warming and then cooling back through the Curie point, this residual pyroelectric signal behaves exactly as it did in Fig. 2. Thus, the direction of the current above the Curie point appears to be independent of the direction in which the crystal was originally polarized at room temperature.

These observations demonstrate that an appreciable polarization persists in the crystal well above the Curie point, even though no external field is applied. A calculation shows that it is quite impossible for the polarization to be produced by residual strains in the crystal at temperatures of 20°C or more above the Curie point. The most plausible hypothesis is that this polarization

is caused by space-charge fields inside the crystal. The experiments to be described below support this interpretation and also demonstrate some of the consequences of the space-charge fields.

OBSERVED WAVE FORMS

On going through the Curie point, the wave forms of the signals fed into the amplifier undergo considerable changes. The light chopper gives rise to trapezoidal-shaped light pulses, which in turn, give rise to trapezoidal-shaped pyroelectric current pulses at the source. Below the Curie point, these wave forms reach the amplifier input without distortion. A typical pulse shape is shown in Fig. 5(a). From a few degrees above the Curie point to the highest temperatures reached in these experiments, the wave form commonly appeared as in Fig. 5(b); this is the high transient current discussed earlier and it suggests the differentiation of an approximately square voltage pulse. Above the Curie point, a third type of wave form was frequently encountered; it is shown in Fig. 5(c). It suggests a combination of the wave forms in Figs. 5(a) and 5(b).
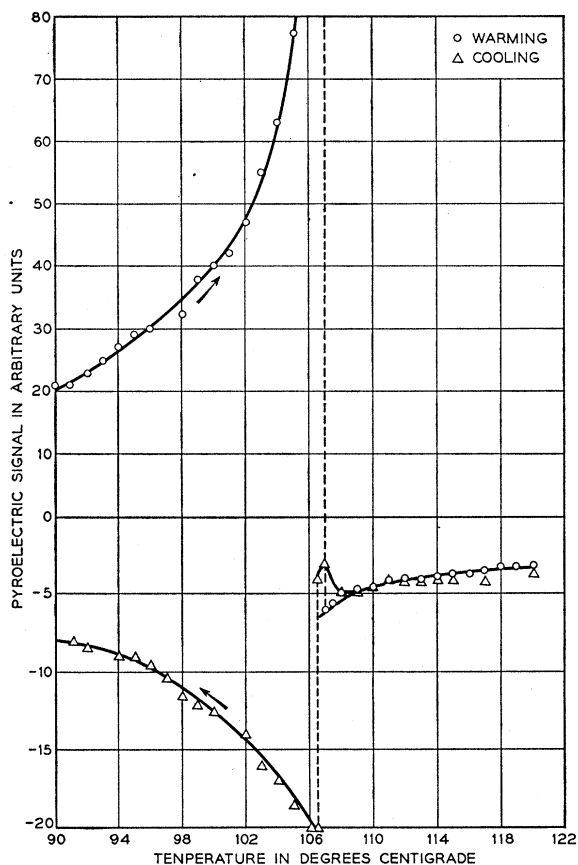

FIG. 4. A plot taken in the same way as that of Fig. 2, the crystal having been polarized previously with a saturation *positive* field.
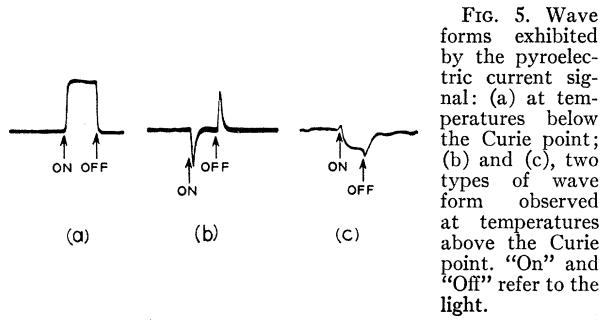
FIG. 5. Wave forms exhibited by the pyroelectric current signal: (a) at temperatures below the Curie point; (b) and (c), two types of wave form observed at temperatures above the Curie point. "On" and "Off" refer to the light.

EQUIVALENT CIRCUIT

To understand these observations, it is necessary to consider an equivalent circuit that describes the features of the crystal, its barrier layers, and the input impedance to the amplifier. Assume that at each of the two major faces of the crystal a space-charge layer exists. Above the Curie point, these layers possess an appreciable polarization while that of the bulk crystal is zero. An equivalent circuit is shown in Fig. 6. The parallel combinations C_{B1}, R_{B1}, and C_{B2}, R_{B2}, represent the barrier capacitances and resistances. The parallel combination C_X, R_X represents the bulk crystal between the space-charge layers. When the crystal is illuminated, both barrier regions will act as signal generators but the surface facing the radiation will change temperature more rapidly than the other barrier and consequently, will give, in general, a larger signal.

Consider first, the signal generated in barrier 1. During the light pulse the polarization changes at a constant rate. It is appropriate, therefore, to represent the signal source as a constant current generator of zero

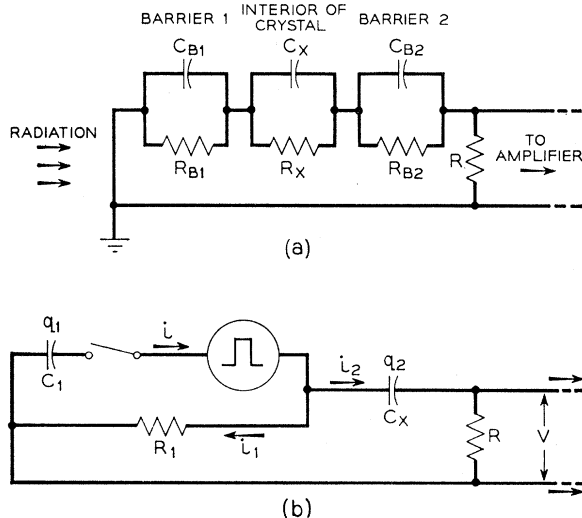BARRIER 1   INTERIOR OF CRYSTAL   BARRIER 2

(a)

(b)

FIG. 6. Equivalent circuits describing the state of the crystal above the Curie point: (a) the complete equivalent circuit representing barriers at each surface coupled by the bulk capacity of the crystal; (b) the reduced equivalent circuit that can be used when short pyroelectric current pulses are produced in one barrier only.

impedance in the capacitative branch of the barrier equivalent circuit. For short current pulses, the dominant impedance in the bulk of the crystal and barrier 2 is either C_X or C_{B2}, whichever is the smaller. It is reasonable to assume that $C_{B2} \gg C_X$. Thus, a reduced equivalent circuit may be drawn as in Fig. 6(b), where C_1, R_1 represent the barrier 1. Let the current generator produce a constant current, i, during the light pulse. Then, using the notation of Fig. 6(b), we have

$$i = i_1 + i_2, \qquad (2)$$

$$i_2 = dq_2/dt, \qquad (3)$$

and

$$i_1 R_1 = -q_1/C_1 = i_2 R + q_2/C_X. \qquad (4)$$

From these equations,

$$\frac{dq_2}{dt} + \frac{q_2}{C_X(R_1+R)} - \frac{iR_1}{(R_1+R)} = 0. \qquad (5)$$

With the condition that $q_2 = 0$ at $t = 0$, the solution of this equation is

$$q_2 = iR_1 C_X \left[1 - \exp\left(-\frac{t}{C_X(R_1+R)} \right) \right]. \qquad (6)$$

Thus, during the light pulse, the signal V generated by the pyroelectric current is

$$V = i\left(\frac{R_1 R}{(R_1+R)} \right) \exp\left(-\frac{t}{C_X(R_1+R)} \right). \qquad (7)$$

Experimentally, light pulses occur at a steady rate and the interval between pulses is not too different to the duration of the pulse. Thus, the temperature of the crystal reaches a dynamic equilibrium such that the rate of warming during the light pulse is not too different to the rate of cooling during a dark interval. Thus, when the light is cut off, a constant current pulse, $-i_D$, is produced, the current flowing in the direction opposite to that during the light pulse. This produces a signal, V_D, where

$$V_D = -\frac{i_D R_1 R}{(R_1+R)} \exp\left(-\frac{t}{C_X(R_1+R)} \right). \qquad (8)$$

Hence, the complete wave form of the signal fed into the amplifier during a light-dark cycle is as represented in Fig. 7. Thus, this equivalent circuit gives rise to the basic wave form that is observed experimentally.

The above considerations can be extended to the situation where signals are generated in both surface layers simultaneously. There are two cases to consider: (a) both barriers polarized in the same direction; (b) the barriers polarized in opposite directions. Making the assumption that $C_{B1} \gg C_X$, as before, it is clear that the barrier 2 sees an effective circuit which is identical to that seen by barrier 1, a capacity C_X in series with resistor R. The signal that appears across R durig an

light pulse acting on barrier 2 alone can be written, therefore,

$$V' = i'\left(\frac{R_2 R}{(R_1 + R_2)}\right) \exp\left(-\frac{t}{C_X(R_2 + R)}\right), \quad (9)$$

where i' is the pyroelectric current generated in barrier 2. In case (a), the net signal U seen at the amplifier input is $V + V'$ whereas in case (b), $U = V - V'$. Hence, the net signal during a light pulse is

$$U = \frac{R}{(R_1 + R_2)}\left[iR_1 \exp\left(-\frac{t}{C_X(R_1 + R)}\right) \right.$$

$$\left. \pm i'R_2 \exp\left(-\frac{t}{C_X(R_2 + R)}\right)\right]. \quad (10)$$

Equation (10) describes the ideal general case of uniform space-charge layers at each electrode. However, under most experimental conditions the signal from one barrier will completely dominate that from the other. This will occur, for instance, when most of the incident energy is used up near the surface of the crystal that faces the light. Alternatively, a barrier may exist at one surface only, or more generally, it may be much more extensive at one surface than the other. In these cases, the signal is adequately described by an equation of the form of (7).

The wave form is more complex if the two barriers give rise to comparable signals. Not only does the signal depend on whether the two currents are in the same or in the opposite direction, but it also depends on the relative magnitudes of R_1, R_2, and R. If R_1 and R_2 are small compared to R, Eq. (10) then takes on the form of (7). However, this approximation may not be always a good one in practice.

There remains the third wave form of Fig. 5 to be considered. Strong space-charge fields at the two surfaces of the crystal will produce, in general, a field over the bulk of the crystal. Two possible potential distributions are indicated in Fig. 8. The field over the bulk of the crystal will be weak compared with the barrier fields, but just above the Curie point it will possess an appreciable polarization owing to the high polarizability of the medium. Thus, a pyroelectric signal will be produced in the bulk of the crystal, that is, in the equivalent circuit C_X, R_X. Owing to the high barrier capacities, the signal will appear as a square voltage pulse rather than in the differentiated form. Again assuming the most likely situation where the signal from one barrier is much greater than that from the other, the net signal is now the summation of a square voltage pulse and an exponentially decaying signal. From Fig. 8 it is clear that the signals arising in barrier 1 and the bulk crystal can be in opposite directions and thus the resultant wave form will be like that shown in Fig. 5(c).

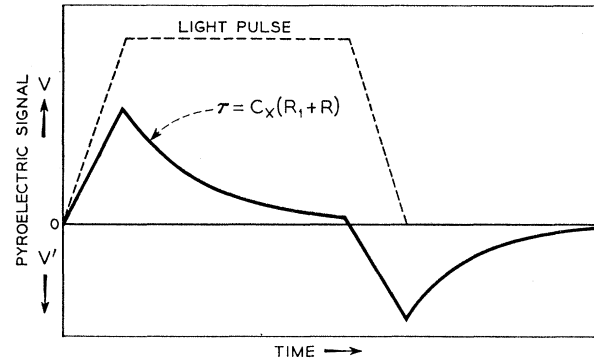Therefore, the equivalent circuit that has been used

Fig. 7. Wave form to be expected for short pyroelectric current pulses produced in either barrier alone, based on the equivalent circuit of Fig. 6(b).

is capable of explaining the various wave forms observed and at the same time, the circuit applies to a realistic model for the crystal with space-charge barriers. A closer comparison was made as follows: From Eq. (7) the signal seen by the amplifier decays with a time constant, τ, of $C_X(R_1 + R)$. Thus, if $R_1 < R$, τ is a linear function of R. Measurements were made of τ as a function of R over as wide a range of R as possible. The lower limit of R was governed by the decrease in amplitude of the signal; the upper limit was the amplifier input impedance. The results are plotted in Fig. 9, where it will be noted that, to within experimental error, τ varied linearly with R, as predicted. The slope of the line gives C_X, the effective bulk capacity of the crystal. The value of C_X was ~ 1700 $\mu\mu$f. The capacity of the crystal at the same temperature was measured using a General Radio capacity bridge and applying only a small signal to the crystal. This gave a value of about 1300 $\mu\mu$f. In view of the uncertainties involved, this figure is felt to be in satisfactory agreement with that of C_X, the capacity in the interior of the crystal.
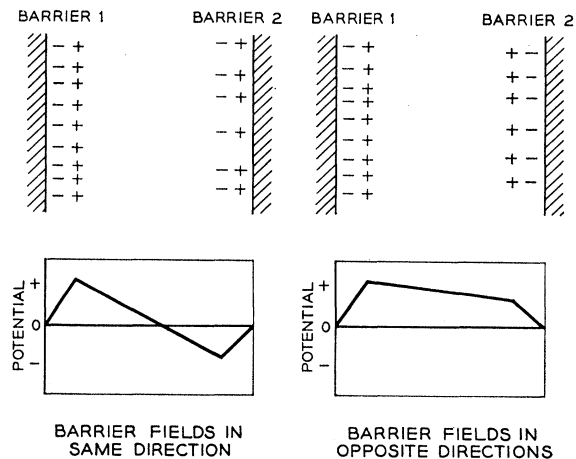

Fig. 8. Indicating the manner in which space-charge fields at the surfaces may give rise to a field in the interior of the crystal.
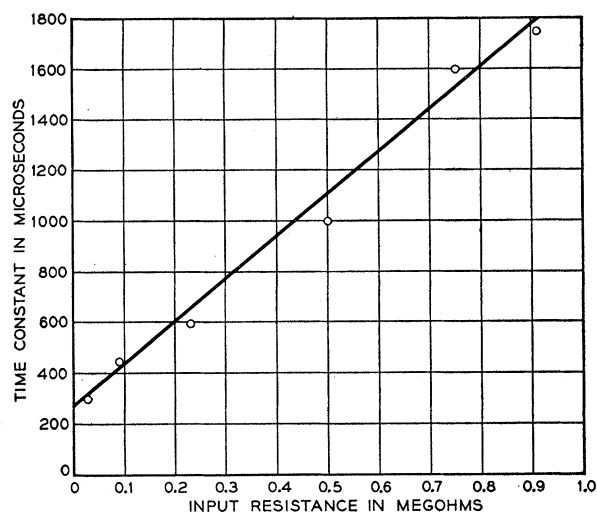
FIG. 9. The time constant for decay in the wave forms of type 5(b) plotted against the input resistor.

Furthermore, the capacity at the same temperature was calculated assuming a dielectric constant of 8000, the crystal having a thickness of 4.5×10^{-3} cm and the electrode diameter being 0.9 mm. These figures give a value of 1000 $\mu\mu$f for the capacity, again in reasonable agreement with the above values. When $R=0$, the time constant $\tau_0 = C_X R_1$. From Fig. 9, $\tau_0 = 270\mu$ sec. Putting $C_X = 1700$ $\mu\mu$f, this gives R_1, the effective barrier resistance as measured by dc, a value of 1.6×10^5 ohms. If the barrier conductivity were known, its thickness could be determined. If one makes the admittedly crude assumption that the barrier conductivity is comparable to that of the crystal as a whole, the latter having been measured to be about 3×10^{-9} mho/cm at the temperature of the above experiments, the barrier thickness is estimated at $\sim 3 \times 10^{-5}$ cm, which is a not unreasonable value.

From the experimental results and discussion given above, it is concluded that the existence of space charge layers in the crystal above the Curie point has been demonstrated. Next, it was of interest to study in more detail the effect of temperature on the space charge layers.

TEMPERATURE VARIATION OF BARRIER-LAYER PYROELECTRIC CURRENTS

If the distribution of charges responsible for the potential barriers can be altered in any way, the barrier pyroelectric signal should show a change. An obvious line to follow was the effect of raising the temperature considerably above the Curie point.

The variation of the pyroelectric signal with temperature is shown in Fig. 10. The points represent the height of the initial peak in wave forms of the type 5(b). Referring to Eq. (7), at $t=0$, this peak height is proportional to the true pyroelectric current, i. On the

temperature scale of Fig. 10 the Curie point occurred just below 105°C. Immediately above the Curie point, the signal started at its highest value. As the temperature increased up to 134°C, the signal steadily decreased. On cooling again to the Curie point, the signal showed a smooth increase but along a much lower path to that while warming. On raising the crystal temperature to 152°C, the signal again steadily decreased. Holding the temperature steady at 152°C for half an hour resulted in a further decay of the signal. On subsequent recooling to the Curie point, the signal followed a much lower path. Thus, it is clear that the situation that produced the pyroelectric signal was largely "annealed out" of the crystal by the temperature cycling. It is reasonable to assume that during the annealing process, the cubic phase in the interior of the crystal grows at the expense of the tetragonal phases of the surface layers. Thus, the thickness of the barrier is decreased by the annealing. This decrease can be represented in Eq. (7) by a decreasing value of the barrier resistance R_1 and it is clear that as R_1 decreases, the signal height also decreases. As R is greater than R_1, in general, the annealing does not produce any great change in the time constant.

Though the barrier thickness is decreasing during the annealing, the space-charge potentials will remain roughly the same. Thus, the field in the barrier increases though this is not expected to affect the amplitude of the signal to any great extent, particularly for such high fields and at temperatures well above the Curie point. The space-charge field acting on the cubic phase in the bulk of the crystal will vary only slightly during the annealing. Consequently, at all stages of the annealing, an approximately constant square voltage pulse will appear at the amplifier input due to the pyroelectric signal generated in the cubic phase. Before annealing, the signal produced in the barrier may be considerably larger than that produced in the bulk and consequently, the signal has a wave form very much like Fig. 5(b). After annealing, only the signal produced in the bulk of the crystal will be present and consequently, the signal observed will be a square pulse. This transformation in the pulse shape during annealing was observed experimentally and thus provides further evidence for the above model of the crystal.

RECOVERY OF BARRIER LAYER SIGNAL

After annealing above the Curie temperature, the crystal was cooled to room temperature at which a strong field was applied for several minutes. After removing the field, the crystal was taken to above the Curie point again and it was observed that the crystal behaved as if it were still annealed. This was verified over several runs, and in no case was it found that a field applied below the Curie temperature noticeably undid the effect of the annealing. This was true for

either sign of the field and for application times of up to 30 minutes at temperatures lower than 85°C.

If, after annealing, a field was applied to the crystal at a temperature above the Curie point, the barrier signal was recovered. That is, after applying the field for a short period and then removing, it was found that the signal was returned to its original amplitude and shape. The time factor in the field application was relevant as the recovery of the barrier signal exhibited an appreciable relaxation time depending primarily on the field strength. On removing the field, there was again an appreciable time lag before the field-induced pyroelectric signal decayed leaving only the barrier pyroelectric signal. The barrier signal was recovered for either direction of the field but, surprisingly, the sign of the barrier signal was independent of the sign of the field. Furthermore, the application of the field did not affect the sign of the square pulse obtained from the pyroelectric signal generated in the bulk of the crystal. In terms of the model used above it would seem that the effect of the field, whatever its sign, was simply to increase the barrier width while not affecting the direction of the barrier field. More detailed investigations would be required to fully explain this behavior, though it is possible that the main role of the applied field in recovering the barrier signal is to apply a stress. In this case, the effect would be the same for either direction of the applied field; the resulting strains could cause the barrier region to grow at the expense of the cubic phase.

It was verified that the cycle of annealing and recovery of the barrier signal could be repeated indefinitely. This behavior was observed qualitatively in several crystals, though it varied considerably in degree. In some crystals the annealing was quite rapid at temperatures only a little above the Curie point while in other crystals, prolonged heating at a temperature of about 170°C was required to effect any annealing.

CAPACITY MEASUREMENTS DURING ANNEALING

The capacity of the crystal as a whole was measured at 1 kc/sec during the annealing process. First, at a temperature just above the Curie point, the barrier pyroelectric signal was obtained by applying a strong field for a minute. After removing the field, the capacity of the unit was measured while the temperature was raised slowly to 170°C. After holding the crystal at this temperature for half an hour, the temperature was slowly lowered, capacity readings again being taken. To within experimental error, the readings repeated those taken while warming. Having regained the original temperature just above the Curie point, a check on the pyroelectric signal showed that annealing had taken place. The temperature being held steady, a field was applied to regain the barrier signal. Again there was no appreciable change in the capacity. These observations tend to confirm the equivalent circuit model, since the
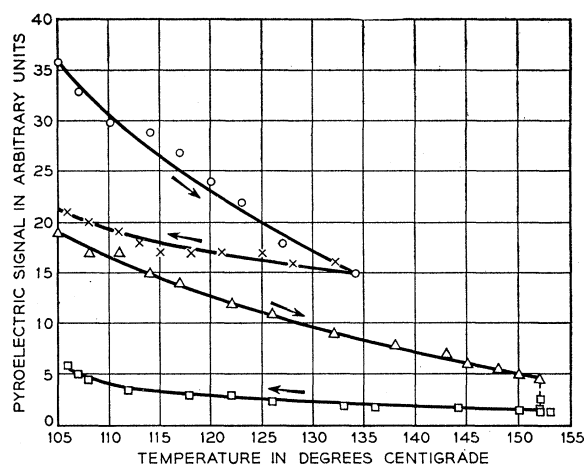

FIG. 10. Variation of the pyroelectric current with temperature cycling above the Curie point. The data demonstrates the annealing effect that takes place.

annealing affects the barrier capacities rather than the bulk capacity.

PHOTOVOLTAIC EFFECT

As already discussed, a weak photovoltaic effect was found to occur with the barrier pyroelectric signal. That is, with no field applied to the crystal, a *steady* photocurrent could be drawn. At a temperature just above the Curie point, a field was applied so as to produce the barrier pyroelectric signals. On removing the field, the crystal was illuminated with light of wavelengths longer than 6100 A and steady currents were obtained.

Measurements were made of the photovoltaic current and the barrier pyroelectric current as the crystal was put through an annealing cycle. A field was applied to the crystal for a minute at a temperature just above the Curie point. Afterwards, the crystal temperature was raised slowly up to 160°C where it was kept for 15 minutes before cooling, measurements again being taken. During this cycle alternate readings were taken of the photocurrent, using a dc electrometer, and the pyroelectric signal measured on the oscilloscope. The results are shown in Fig. 11. It will be noted that the two currents show much the same behavior through the cycle.

The occurrence of a photovoltaic effect is further direct evidence of the presence of potential variations through the crystal. From the parallel behavior of these currents and the pyroelectric currents as shown in Fig. 11, it is concluded that the photovoltaic effect is directly associated with the barriers responsible for the pyroelectric signals, though it is not proposed to discuss any detailed mechanism here.

EFFECT OF BARRIER LAYERS ON NET
POLARIZATION OF THE CRYSTAL

It was pointed out in connection with Figs. 2 and 4 that when the crystal was cooled through the Curie
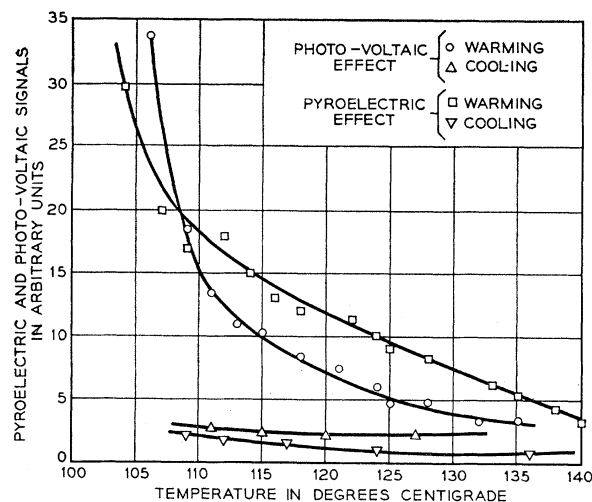
FIG. 11. The photovoltaic current plotted with the pyroelectric current as the crystal was taken through an annealing cycle. The current scales have been roughly normalized.

point with no applied field, a pyroelectric signal appeared whose amplitude was a large percentage of that obtained when the crystal was completely polarized in one direction. Ideally, these crystals possess very large numbers of c-domains which can orient themselves in either of the two directions. If there is no interaction between domains and no other influences present, it is clear that on cooling through the Curie point, the general result will be that approximately equal numbers of domains line up in opposing directions. In this case both the net polarization and pyroelectric current will be zero. It would take an impossible statistical fluctuation to give rise to, reproducibly, the pyroelectric currents observed. It is clear, then, that the direction in which the domain polarizes must be biased in some way. It is reasonable to associate this bias with the presence of the barrier layers.

Some experiments were made to see whether this "built-in" bias could be changed. The method was primarily that of measuring the pyroelectric currents just above and just below the Curie point as the crystal temperature was alternately raised and lowered through the transition. An electric field was applied, when desired, while the crystal was several degrees below the Curie point and its effect, if any, on the pyroelectric signals at the transition was noted. At the same time,
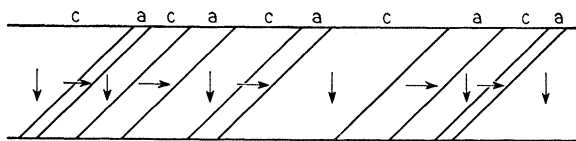

FIG. 12. The type of domain pattern that appears when the crystal is cooled through the Curie point with no field applied, as deduced from observations of the pyroelectric signals and Barkhausen pulses that appear at the transition.

the signs of the "Barkhausen-type" pulses at the transition were noted. These pulses occur when the domains spontaneously polarize or depolarize. In Table I is summarized some typical data. It will be noted that after positive voltages were applied, the pyroelectric signal on warming through the Curie point averaged around +100 while after negative fields it averaged about the same value in the opposite direction. This is the behavior to be expected if saturation polarization is attained by the applied field. However, no matter what the sign or magnitude of the field, the pyroelectric signal that appeared on cooling through the transition was always around −45. Thus the application of fields below the Curie point did not appear to affect the orientation bias in the crystal. This compares with the ineffectiveness of such treatment for recovering the barrier layer pyroelectric signals. Similar results were found to hold for several crystals though there were a few exceptions where it was sometimes possible to

TABLE I. The behavior of the pyroelectric signal and the Barkhausen-type pulses at the Curie transition after applying various fields to the crystal at temperatures below the transition. The pyroelectric signal recorded while warming and cooling through the Curie point is its maximum value immediately below the transition.

Voltage applied below T_c	Pyroelectric signal just below T_c		Sign of Barkhausen pulses on cooling through T_c
	Warming through T_c	Cooling through T_c	
+20	+105	−35	+
+20	+ 90	−45	+
+20	+100	−45	+
−20	−105	−45	+
−20	−100	−50	+
+200 (1¼ hr)	+110	−30	+
+200 (1¼ hr)	+100	−40	+
−200	− 95	−40	+

affect the bias by means of applied fields. Also recorded in Table I are the signs of the Barkhausen pulses observed on cooling through the Curie point. Those crystals which showed a pronounced bias in the direction in which they polarized exhibited Barkhausen pulses almost entirely of one sign. Certainly the ratio of positive to negative (or vice versa) pulses was greater than 100:1. This asymmetry was interpreted as indicating that a considerable number of a-domains was created on cooling while the rest of the crystal consisted of c-domains oriented all in the same direction, as shown in Fig. 12. In this way one can account for the reduction in the net pyroelectric signal compared with its value when the whole of the crystal is c-domained and polarized in one direction. Furthermore, the spontaneous formation of the configuration of Fig. 12 will give rise to Barkhausen pulses of one sign only. An additional check was made by examining the crystals in polarized light after cooling; large numbers of a-domains were found to be present even though the

crystal was mostly c-domained before warming. The foregoing electrical measurements thus confirm the well-known domain patterns that have been observed by optical means.

Some observations were made on one crystal to see whether annealing it affected the way in which it polarized on cooling. The pyroelectric signal was noted on cooling both before and after an annealing treatment. It was found that the annealing did, in fact, reduce the size of the signal by a factor of about 3. Also, after annealing, about equal numbers of positive and negative Barkhausen pulses were observed, suggesting that the crystal was approximating a c-domain distribution with a zero net polarization.

ASYMMETRICAL HYSTERESIS LOOPS

It has been shown elsewhere that when the field applied to the crystal is cycled between suitable limits the pyroelectric current follows a hysteresis loop.[3] In general, these loops are found to be considerably asymmetrical with respect to the origin of the axes. Not only is the coercive force different in the two directions, but so is the "remanent" pyroelectric current at zero field. Such a loop is shown in Fig. 13. The presence of space charge layers provides a ready explanation for this effect. Suppose the space charge produces a field, E_s, over the bulk of the crystal. The field in the barrier is much higher than the fields, E, applied externally to the crystal so that the direction of polarization of the barrier layer remains fixed. If the true coercive force for the crystal is E_c, the external field required to switch the interior of the crystal will be $E_c \pm E_s$ and thus will be different in the two directions. This accounts for the asymmetry along the field axis. Similarly, the net pyroelectric signal depends on the algebraic sum of the contributions from the regions polarized in different directions. The barrier layer signal approaches the square wave form at room temperature since, as has been determined experimentally, the resistivity of the crystal (and therefore R_1) is of the order of a thousand times its value above the Curie point, while the capacity, C_x, varies by somewhat less than two orders of magnitude. If the barrier layer contributes a signal I_B while the bulk of the crystal contributes a signal I_x, the net signal will be $I_B \pm I_x$, depending on the direction of polarization of the bulk of the crystal. This will account for the asymmetry of the loop along the pyroelectric current axis.

It has been noted above that the relaxation time for adjustment of the space-charge fields varies considerably from crystal to crystal. In some crystals space charge fields can be set up quite rapidly even at room temperature; this leads to the following behavior. At positive saturation fields the pyroelectric current signal is in the positive direction. Normally, on removing the field, the pyroelectric current remains about the same due to the remanent polarization at zero net field. If,
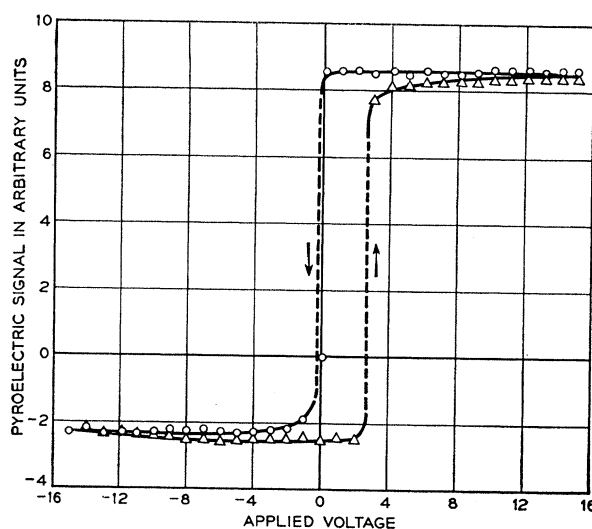

FIG. 13. Asymmetrical hysteresis loop as determined from pyroelectric current measurements.

however, a positive field very much larger than the coercive field is applied for a few minutes and then removed, the pyroelectric signal swings over into the negative direction. This can occur only if, on removing the external field, there remains a net negative field. Thus, while the high positive field is applied, an opposing space charge field builds up in the crystal. If this space-charge field is greater than the coercive force it is able to switch the domains when the positive field is removed, thus causing a change in the sign of the pyroelectric current. The space charge fields set up in this way were not very stable, usually decaying to zero in a few minutes at room temperature. This behavior is portrayed in Fig. 14. After applying +20 volts to the crystal for 15 minutes, the voltage was dropped to +15 followed by a point-by-point plot of the pyroelectric signal as the field was cycled to −15 volts and back. The whole cycle took about 10 minutes.
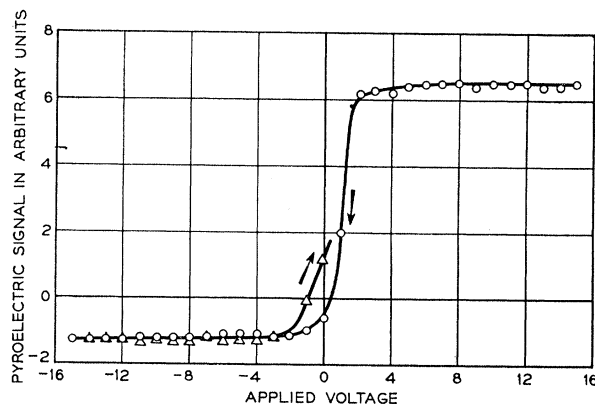

FIG. 14. Hysteresis loop traced in the "reverse" direction due to the action of space-charge fields induced by the application of strong external fields.

It will be seen that as the positive voltage was reduced the pyroelectric signal swung negative before the field reached zero. Thus, at this stage the space-charge field was still sufficient to switch the crystal. Proceeding to negative fields, the pyroelectric signal saturated in the negative direction. On reducing the negative field, the crystal again switched before the field reached zero, indicating that the negative field had replaced the original space-charge field by one in the opposite direction. In this way the crystal could be made to behave as if it traced its hysteresis loop in the reverse direction. This behavior was verified in several crystals where it differed only in scale and in relaxation times.

CONCLUSIONS

The occurrence of small pyroelectric signals at temperatures well above the Curie point indicates that the crystal remains polarized, at least, in some regions. This polarization is believed to be due to a space-charge field residing at the surface layers of the crystal. The pyroelectric signals generated in these layers are coupled to the amplifier, in effect, by the bulk capacity of the crystal. Under certain operating conditions this coupling gives a distorted rendering of the square current pulse as produced at the source. An equivalent circuit is proposed which proves useful in the interpretation of the wave forms observed and for understanding the state of the crystal.

The magnitude of the pyroelectric effects due to the barrier fields varied considerably from crystal to crystal though the effects were present in all crystals investi-gated. Often the barriers could be modified by suitable heat treatment but were returned to their original condition when fields were applied above the Curie point.

From the experiments described in this paper, no information can be gathered on the nature of the potential barriers. It is not known, therefore, whether the barriers arise from impurity ion distributions or from trapped electrons or positive holes.

On cooling the crystal through the Curie point, the pyroelectric signals indicate that the crystal usually shows a decided bias for the direction in which it polarizes. This bias persists at room temperature and is probably responsible for the fact that the pyroelectric hysteresis loops are almost always asymmetric in both current magnitude and applied field. It is apparent that such biasing fields in crystals above the Curie point will influence electrical measurements of the dielectric constant and associated parameters. This may explain some of the difficulties that have been encountered by other workers when making capacity measurements above the Curie point. Yet another effect of the biasing fields will be to cause an apparent shift in the Curie temperature; it will show variations from crystal to crystal owing to the varying space charge field strengths. If these are strong enough, the crystal may appear to go through a second-order type of transition at the Curie point. Finally, it is to be expected that the barrier layers at the surface will have some bearing on the way in which new domains nucleate when the crystal is being switched.