

(3) Such complex spectra may occur in cubically octahedral environments as well when the external field is not along a direction corresponding to a principal axis of the hfs tensor and if the hfs is anisotropic.

(4) This critical re-examination of the Mn⁺⁺ZnF₂ system should be extended to that of Fe⁺⁺ and Co⁺⁺ before the F¹⁹ hfs may be interpreted for similar effects which will be present in these two cases.¹

Furthermore any "first principles" calculation of the magnitudes of the respective F¹⁹ hfs constants must, for other than the isotropic contribution, take into ac-

count the low symmetry about the central ion in the ZnF₂ host lattice.

We have demonstrated that there exists very good agreement between the measurements made herein and shifts of the NMR of F¹⁹ observed in paramagnetic and an antiferromagnetic MnF₂.

ACKNOWLEDGMENTS

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Pyroelectricity, Internal Domains, and Interface Charges in Triglycine Sulfate

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Using the dynamic pyroelectric technique, the spontaneous polarization of triglycine sulfate has been determined between the Curie point and -140°C . No evidence of any phase transitions over this temperature range was found (other than the Curie point). The polarization could still be reversed by an applied field, though slowly, at the lowest temperatures attained. In the paraelectric region above the Curie point, the pyroelectric behavior shows some deviations at low applied fields from the predictions of Devonshire's theory. The cause of these deviations is not known but they may be due to nonuniform conditions, either mechanical or electrical, in the crystal.

With no field applied to the crystal, pyroelectric signals can be generated temporarily above the Curie point. These are ascribed

mainly to polarizations induced by the compensation charges while they last, which accumulate around residual domains that cannot be removed by the poling field at room temperature. These residual domains have been delineated using powder pattern and etching techniques and are revealed as long thin domains, pointed at both ends and lying along the ferroelectric direction, either in the interior of the crystal or intercepting the surfaces. The causes of these persistent domains are not known.

It is found that on cooling a crystal through the Curie point, there is a strong tendency for it to repolarize with the same polarity it had previously. This phenomenon is ascribed to the presence of ferroelectrically inactive surface layers giving rise to interface charges.

INTRODUCTION

THIS paper is concerned with a pyroelectric investigation of the ferroelectric crystal triglycine sulfate, using techniques that have been described in detail elsewhere.¹⁻³ The spontaneous polarization has been determined down to -140°C and the pyroelectric properties of the crystal in the paraelectric region above the Curie point have been studied and compared with the predictions of Devonshire's theory.⁴ In addition, small pyroelectric signals have been observed above the Curie point when no external field is applied and the probable origins of these are discussed in some detail. Furthermore, evidence for surface layers is found from studies of the repolarizing of the crystals on cooling through the Curie point.

EXPERIMENTAL

Thin slices cleaved from a parent crystal of triglycine sulfate were etched in water until they were about 10^{-2}

cm thick. Units about 3 mm square were cut from these etched slices and provided with circular evaporated gold electrodes, about 2 mm in diameter. For some of the studies, units were provided with a guard-ring electrode so as to avoid possible spurious results arising from the effects of fringing fields; these have been shown to be appreciable under certain conditions.⁵

The crystals were mounted in an oven, the temperature of which was indicated by a thermocouple that fed into the *Y* axis of an *X-Y* chart recorder. The chopped light beam used for generating the pyroelectric signal reached the crystal through a small window in the oven wall and the pyroelectric signal, after amplification and rectification, was applied to the *X* axis of the recorder. As the light falling on the crystal made its temperature slightly higher than that of the oven (by about 5°C), the thermocouple readings were corrected so as to bring the Curie point to 49.8°C , where appropriate.⁶

¹ A. G. Chynoweth, *J. Appl. Phys.* **27**, 78 (1956).

² A. G. Chynoweth, *Acta Cryst.* **10**, 511 (1957).

³ A. G. Chynoweth, *Phys. Rev.* **102**, 1021 (1956).

⁴ A. F. Devonshire, *Phil. Mag.* **40**, 1040 (1949).

⁵ R. C. Miller and A. Savage, *J. Appl. Phys.* **30**, 808 (1959).

⁶ S. Triebwasser, *IBM J. Research Develop.* **2**, 212 (1958).

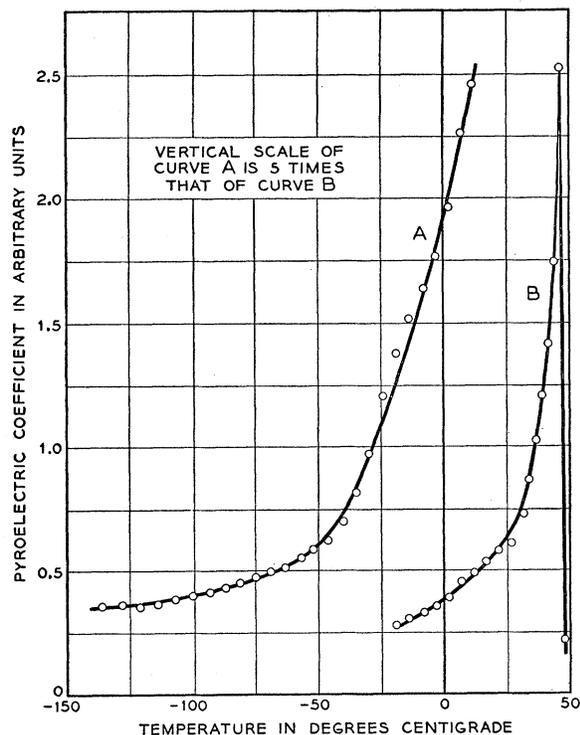


Fig. 1. The pyroelectric signal *versus* temperature.

RESULTS

A. Spontaneous Polarization *versus* Temperature

The crystal was first polarized at room temperature with a steady field of $\sim 10^3$ volt cm^{-1} applied for several seconds. The field was then removed, the crystal cooled, and the pyroelectric signal determined as a function of temperature from -140°C up to the Curie point (Fig. 1). As the signal is proportional to the product of the specific heat and the pyroelectric coefficient, (dP/dT) , integrating beneath the curve yields the temperature dependence of the spontaneous polarization, in arbitrary units, if the temperature dependence of the specific heat is also taken into account. The curve

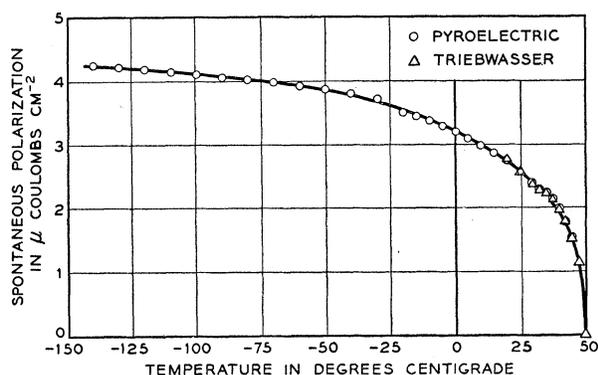


Fig. 2. The temperature dependence of the spontaneous polarization as deduced from the pyroelectric data.

so arrived at was then fitted to the data that have been given for the temperature range between 25°C and the Curie point by Triebwasser.⁶ It will be noted from Fig. 2 that the fit is quite satisfactory, thus demonstrating the validity of the pyroelectric technique. It is also clear that there are no phase transitions other than the Curie point in the temperature range covered. It was found that at the lowest temperatures, the direction of the spontaneous polarization could still be reversed though the reversal took several seconds at field strengths of the order of 10^3 volt cm^{-1} .

B. Pyroelectric Behavior in the Paraelectric Region

At temperatures above the Curie point, the field induced pyroelectric signal was studied as a function of the field strength using the *X-Y* recorder. Figure 3 shows three typical curves traced directly from the recorder chart, these curves being taken on the first excursion made through the Curie point by the crystal. There is a noticeable asymmetry in the curves about the zero of the field but this could be ascribed completely to a residual pyroelectric signal (with no applied field) persisting above the Curie point. It was found that these residual signals gradually disappeared if the crystal was held at a temperature a few degrees above the Curie point for a few minutes. When they had disappeared the pyroelectric signal *versus* field curves became symmetrical about the zero of field and a set of such curves (for one sign of the field only) is shown in Fig. 4, the curves being taken at intervals as the crystal cooled slowly. The absence of any discontinuities in these curves confirms that the Curie point transition is of the second order type.^{1,4} At temperatures sufficiently above the Curie point, the curves approximate straight lines except at the lowest fields. The straight lines are predicted by Devonshire's theory⁴ as long as the polarization, P , is not too large. The free energy of the crystal is written as:

$$F = A(T - T_0)P^2 + BP^4 + CP^6 - E_a P, \quad (1)$$

where A , B , C are positive coefficients, T is the temperature, T_0 is the Curie temperature, and E_a is the applied field. As $(\partial F/\partial P) = 0$, we obtain:

$$E_a = 2A(T - T_0)P + 4BP^3 + 6CP^5, \quad (2)$$

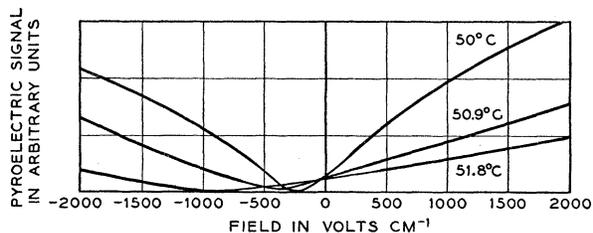


Fig. 3. The field-induced pyroelectric signal *versus* the applied field at temperatures slightly above the Curie point. These curves were obtained while the "residual signal" was still present.

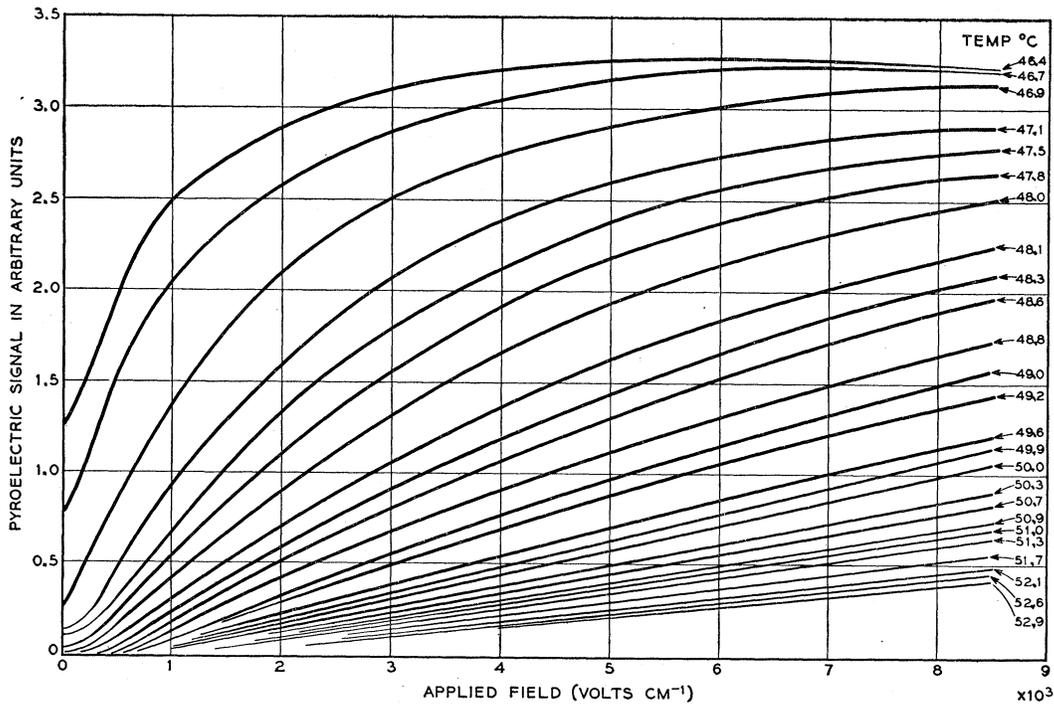


FIG. 4. The field-induced pyroelectric signal *versus* the applied field at various temperatures above the Curie point, after the "residual signal" had been annealed out.

and

$$(dP/dT) = -AP/[A(T-T_0) + 6BP^2 + 15CP^4]. \quad (3)$$

Using published values for the coefficients⁶, some theoretical curves of (dP/dT) *versus* E_a were computed and these are shown in Fig. 5 where it will be seen that, except at the lowest fields, there is fair agreement between the general *shapes* of the experimental and theoretical curves. Equations (2) and (3) also predict that at low values of P , the shape of (dP/dT) *versus* E_a varies as $(T-T_0)^{-2}$, a Curie-Weiss type of law. The plot shown in Fig. 6 is deduced from the straight portions of the recorder curves and is reasonably linear though the extrapolated value for the Curie point, $T_0=44^\circ\text{C}$, is appreciably lower than any that can be arrived at by inspection of Fig. 4. In the next section shifts in the Curie point to lower temperatures as a result of heat treatment will be described; and as the crystal is of necessity subjected to similar heat treatment in obtaining the data for Figs. 3 and 4, the low extrapolated transition temperature is tentatively ascribed to the heating effects. It might be queried also whether changes wrought by heating are responsible for the deviations of the curves in Fig. 4 from straight lines at low fields, namely, in the region where Devonshire's theory predicts good linearity. At first sight, by involving effects due to heat treatment, one could account for both the low-field deviations and the steady deterioration in the sharpness of the Curie point transition (see next section) on the basis of the formation of a spectrum of Curie points in the crystal.

However, this explanation for the deviations is untenable since they occurred immediately when the crystal

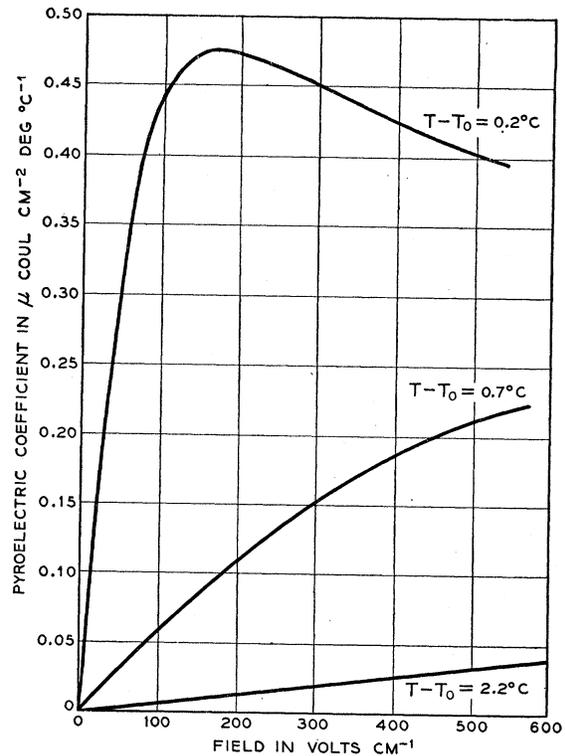


FIG. 5. The field-induced pyroelectric coefficient *versus* the applied field as deduced from Devonshire's theory.

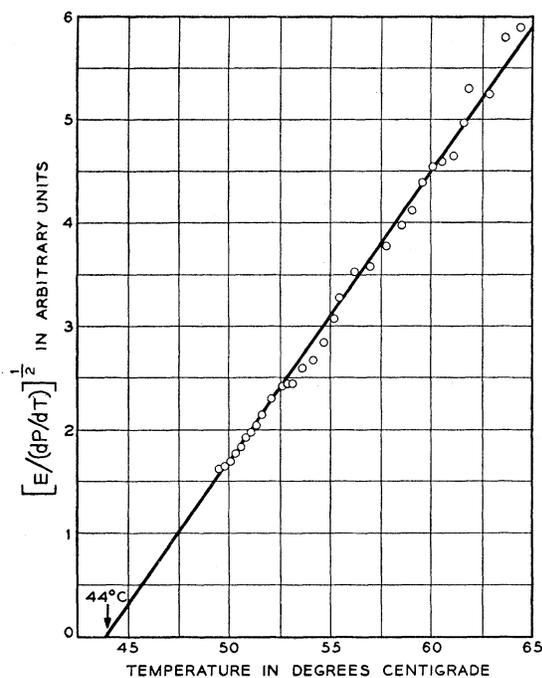


FIG. 6. A linear plot, as predicted by Devonshire's equation, obtained by analysis of the curves of Fig. 5.

was taken, even slightly, above the Curie point for the first time and persisted to the highest temperatures used. Furthermore, at a constant field and temperature, there was no drift in the pyroelectric signal. Various checks that were made showed that the deviations were not caused by instrumental nonlinearities. It is possible that the deviations are related in some way to field-dependent properties of surface layers of the sort to be discussed in the next section.

C. Residual Signal Above the Curie Point

Mention was made in the foregoing of the occurrence of small pyroelectric signals at temperatures appreciably higher than the Curie point. These recall similar observations in barium titanate⁷ where they were ascribed to space charge layers inducing a sizeable polarization in the surface layers of the crystal. Typical behavior of the residual pyroelectric signals in crystals of triglycine sulfate when taken through a heating and cooling cycle is shown in Fig. 7. As the temperature of the previously polarized crystal is raised through the Curie point, the pyroelectric signal passes through the sharp peak and after dropping rapidly through zero it builds up again but in the opposite direction (the figure shows the rectified signal). As the temperature continues to rise, this signal passes through a maximum and then decays to zero within a few minutes. If the temperature is then lowered, the residual signal does

⁷ A. G. Chynoweth, Phys. Rev. **102**, 705 (1956).

not reappear and the pyroelectric signal behaves in a more normal way, remaining approximately zero until the Curie point is approached. The cause of the residual signal has thus been "annealed out". All the crystals investigated exhibited residual signals and in each case these signals could be annealed out by holding the crystal temperature at 10 or 20°C above the Curie point for a few minutes. Even the crystals with guard ring electrodes showed similar residual signals indicating that the signals are not caused by fringing effects.

Figure 8 shows the results of some similar heating and cooling cycles on another crystal. (The total time, taken over a heating cooling cycle was typically about 10 to 15 minutes, with the crystal spending only a few minutes above the Curie point.) First the crystal was polarized at room temperature with a negative field. In the ensuing curve, the dip through zero of the pyroelectric signal just above the Curie point shows that the residual signal was in the opposite direction to that of the pyroelectric signal below the Curie point. The crystal was then rapidly cooled before the residual signal had annealed out. The return curve shown in Fig. 8 reveals that the crystal returned to a fully polarized condition even though no field was applied. This phenomenon was quite frequently encountered in these experiments. Next, the crystal was polarized with a positive field and another heating run taken.

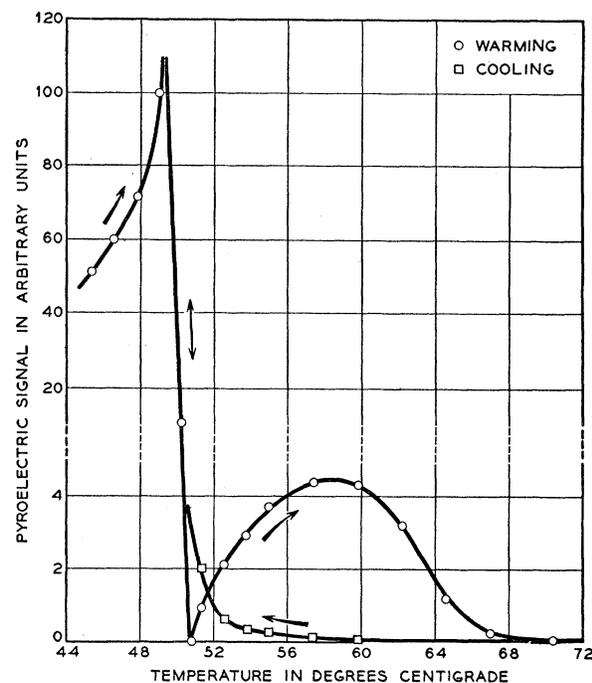


FIG. 7. Pyroelectric signal versus temperature through the Curie point and showing: (i) the residual signal, (ii) the annealing out of the residual signal, and (iii) the return of the crystal to virtually the same polarization condition on cooling. (Note the break in the scale on the ordinate.)

In Fig. 8 it will be seen that in this second heating run, the peak at the Curie point is not nearly as sharp as previously and the position of the peak has shifted to a lower temperature. After the peak the tail in the curve (without any dip through zero) shows that the residual signal has the same sign as when the crystal was initially polarized with a negative field. Hence, applying polarizing fields at room temperature has no effect on the sign of the residual signal.

The deterioration of the peaks noted in Fig. 8 was observed in all samples. With repeated heating and cooling cycles, the peaks became progressively lower and less sharp and moved steadily to lower temperatures. The deterioration was serious if the crystal was taken to about 100°C for a few minutes. This deterioration in the sharpness of the Curie point transition may account for the abnormally low transition temperature predicted by Fig. 6.

Using an asymmetric light chopper, some qualitative observations were made on the sign of the pyroelectric signal and its dependence on field treatments. It was found that the sign of the residual signal was always the same, irrespective of the sign of the poling field applied to the crystal at room temperature. However, its magnitude often appeared to depend on the poling direction; the magnitude of the residual signal was usually greater when its sign was opposite to that of the room temperature pyroelectric signal than when both signals had the same sign.

Applying fields of appropriate sign above the Curie point could cause a temporary change in the sign of the signal but with the field removed, the signal relaxed back faster than the recovery time of the electronic equipment (~ 1 sec) to its original sign.

If no fields were applied above the Curie point, it was always found that when the crystal cooled down through the Curie point, it polarized with the sign appropriate to that of the poling field applied to it briefly at room temperature. On the other hand, if the poling field was applied for several hours at room temperature, then on subsequently heating and cooling the crystal through the Curie point, the crystal repolarized predominantly in the direction opposite to that which resulted from the previous field application.

It was also established that the sign of the residual pyroelectric signal was the same irrespective of which side of the crystal was illuminated.

The annealing effect described earlier was not permanent. If after having annealed out the residual signal the crystal was held at room temperature for several hours, the residual signal could be stimulated again and with the same sign as previously.

In further experiments a fresh, large area cleavage slice, to which no fields had been applied, was used. The macroscopic domain patterns of virgin crystals as revealed by power deposition techniques⁸ are usually

⁸ G. L. Pearson and W. L. Feldmann, *J. Phys. Chem. Solids* **9**, 8 (1959).

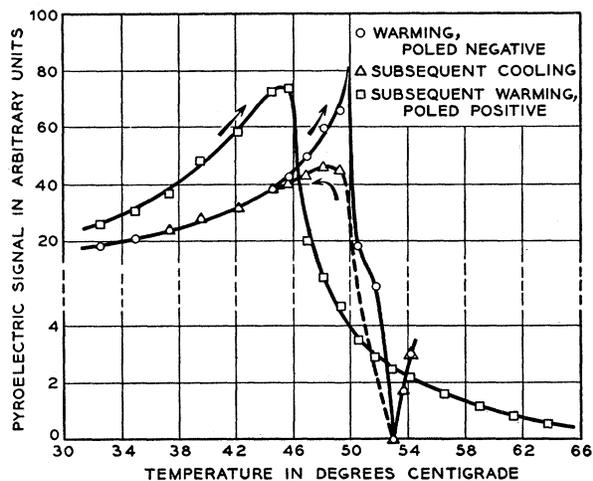


Fig. 8. Pyroelectric signal versus temperature, showing the occurrence of the residual signal after the crystal was poled with either a positive or a negative field at room temperature.

very complex and show little or no order. However, one can often find areas large enough to put electrodes on and over which the spontaneous polarization is almost everywhere in the same direction—this would appear as a uniformly powdered or uniformly clear area. Nevertheless, on closer examination, these apparently uniform areas frequently exhibit fine structure in their powder patterns in the form of randomly scattered local concentrations of powder that give a speckled appearance to the powder pattern. Such speckled patterns have been observed on both virgin crystals and crystals that have been polarized by an applied field.⁹ Typical speckled patterns are shown in Fig. 9 taken at different regions of the same crystal, the same regions having opposite basic polarization directions. A thin over-all covering of powder on the region of appropriate polarization direction accounts for the general background of its picture being darker than that for the other, both photographs having received identical lighting and photographic treatments. As the powder is attracted more strongly to domain walls it is felt that the local concentrations of powder indicate local domain walls. The most obvious conclusion is that there are long narrow domains running right through the crystal (as both sides of the crystal show the speckled pattern) but this is not necessarily so; it has also been found that the external field of a spike-shaped domain stopping far short of the crystal surface is sufficient to cause a local building-up of powder. These spikes can be revealed by powdering the side of the crystal parallel to the ferroelectric axis. Figure 10(b) shows a typical powder pattern taken on the side of a crystal and it is particularly interesting in that it reveals many complete internal domains with shapes rather like circular tooth-picks. Again, the powder pattern reveals more

⁹ A. G. Chynoweth and J. L. Abel, *J. Appl. Phys.* **30**, 1073 (1959). See Fig. 4, for example.

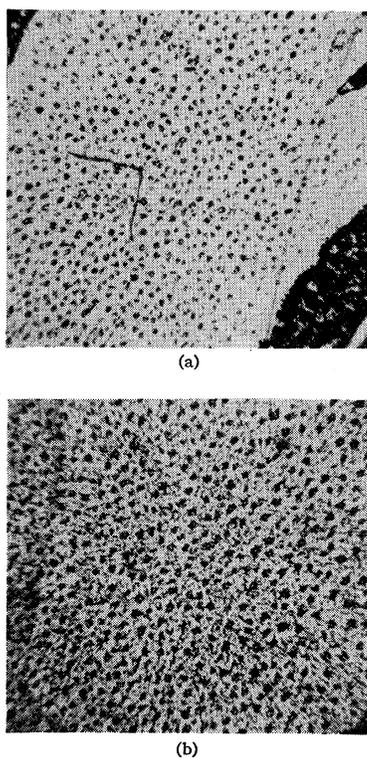


FIG. 9. Power deposition patterns showing fine domain detail in regions of basically uniform polarization. Figures (a) and (b) show two different parts of the same virgin cleavage slice, the two parts having basically opposite polarization directions. The fine detail is present in both regions.

domains than actually intercept the surface whereas only the latter appear to be revealed by etching techniques. The etch pattern corresponding to Fig. 10(b) is shown in Fig. 10(a) (the etch pattern was obtained prior to the powder pattern). The conclusion that both virgin and electrically poled crystals of triglycine sulfate contain many totally internal, long, thin domains, lying along the ferroelectric axis seems inescapable.

Returning to the pyroelectric studies, pairs of electrodes were placed over two regions of a crystal, both regions exhibiting a speckled powder pattern but possessing opposite bulk polarizations. No fields were applied to these electrodes. The sign of the pyroelectric signal below the Curie point was compared with the sign of the residual signal above the Curie point for both regions. It was found that the region with a positive signal below the Curie point showed a negative residual signal and the region with a negative signal below the Curie point showed a positive residual signal. On cooling into the ferroelectric phase again the pyroelectric signals returned with the same sign as previously. The same result was obtained in three repetitions of this experiment with three virgin crystals.

D. Summary of Established Facts Concerning the Residual Signals and the Re-Polarizing of the Crystals on Cooling

1. The residual signal occurs in all crystals and its sign in a particular crystal is not altered by poling fields of either sign applied briefly (at least, up to a few minutes) below the Curie point.

2. The sign of the residual signal is the same irrespective of which side of the crystal is illuminated.

3. The pyroelectric signals induced by brief field applications above the Curie point relax rapidly (in less than a second) leaving the residual signal the same as before applying the field (except for annealing effects).

4. Maintaining the crystal at a few degrees above the Curie point causes the residual signal to disappear within a few minutes. It tends to return, however, with the same sign as previously if the crystal is left at room temperature for a sufficient period (several hours).

5. On cooling the crystal through the Curie point the crystal tends to polarize in the direction appropriate to that of the field *last* applied (briefly) to it and irrespective of whether the residual signal had been annealed out. Occasionally, a crystal repolarizes approximately to saturation. On the other hand, if a poling field is applied for several hours at room temperature, then on subsequent heating and cooling, the

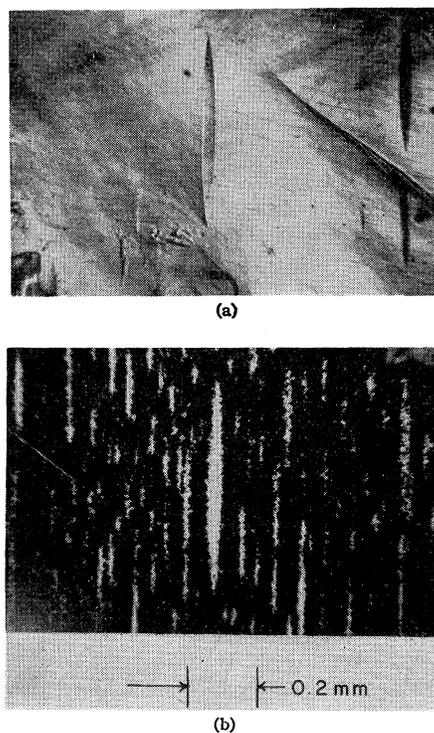


FIG. 10. Domain patterns on the side of the crystal *parallel* to the ferroelectric axis: (a) as revealed by a water etch, (b) as revealed by the powder method.

crystal repolarizes in the direction opposite to that of the field.

6. The sign of the residual signal in virgin crystals is opposite to that of the pyroelectric signal in the ferroelectric phase and on cooling, the crystal repolarizes so as to give rise to pyroelectric signals of the same sign as previously.

Discussion of Residual Signal Effects

It appears feasible to explain the diverse observations on residual signals and re-polarizing effects on the basis of a few plausible assumptions, namely:

(i) Assume that there is a ferroelectrically inactive surface layer, suitably thin, with no (or zero net) spontaneous polarization.

(ii) Imagine rapid formation of a domain structure in which there are, in places, discontinuities in the polarization vectors. Compensation charge will accumulate on these domain boundaries and it will be supposed that this compensation will take place fairly slowly with relaxation times of up to a few minutes. Conversely, this compensation charge will gradually disappear if the spontaneous polarization is suddenly destroyed.

(iii) It will be assumed that there are local regions in the crystal that are strongly pre-disposed to being polarized in a certain direction and that these regions give rise to the long narrow domains which can be either totally internal or can intersect a crystal surface.

As a first step, consider the effect of a field applied to a virgin crystal either in the same or the opposite sense to that of the spontaneous polarization. The imagined condition of the virgin crystal is shown in Fig. 11(a) which also shows the disposition of the *free* charge required for compensation. A field applied briefly in the same sense as the bulk P_s produces no appreciable change in the situation [Fig. 11(b)] but when applied in the opposite sense the bulk P_s is reversed necessitating eventual reversal of the compensation charge at the interface between the bulk of the crystal and the surface layer. This free charge reversal may take place fairly rapidly at first owing to the high fields induced at the electrodes but will then proceed more slowly. At the same time, the compensation charges that were originally around the domains are no longer necessary and these will tend to disappear. Their disappearance may occur slowly at all stages as the net driving field (equivalent to a depolarizing field) that these produce need not be large.

Next, consider what happens when the crystal is taken above the Curie point. The spontaneous polarization disappears everywhere leaving behind the remaining compensation charge. This situation is shown for the two cases in Figs. 11(d) and 11(e). These free charges will give rise to electric fields which in turn will induce a polarization P_1 throughout the bulk of

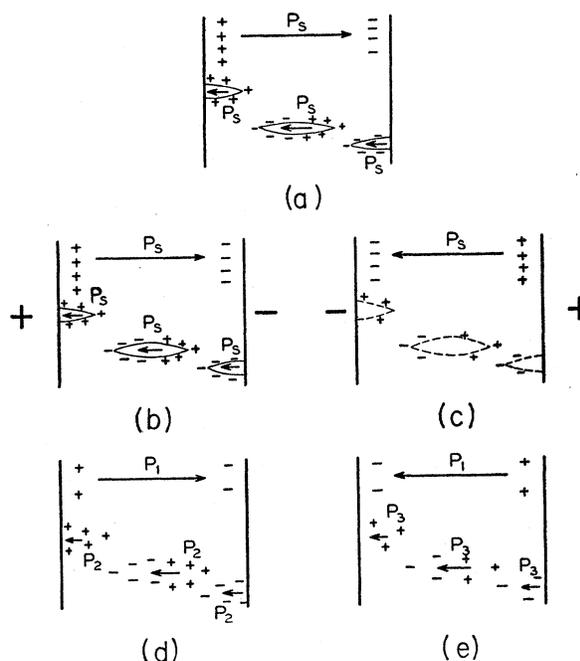


FIG. 11. Proposed model for origin of the residual signals and the tendency for the crystal to repolarize, on cooling through the Curie point, into the same orientation it had previously. All the charges in these figures are free, compensation charges. (a) Virgin crystal containing internal domains and ferroelectrically inactive surface layers. (b) and (c), effect of applying an external field in the same sense and opposing the basic polarization direction, respectively. (d) and (e), the free charge distributions, corresponding to (b) and (c), respectively, which are left when the crystal is taken above the Curie point.

the crystal and net polarizations P_2 and P_3 within the regions formerly occupied by the domains. As the compensation charge around the domains has been dissipating longer in case (c) than in case (b) (since dissipation started when the field was applied at room temperature rather than when the crystal reached the Curie point), P_3 will be somewhat less than P_2 . It will be supposed, however, that the residual pyroelectric signals for which P_2 and P_3 are responsible are much greater than that caused by P_1 . In other words, the fields persisting *within* the old domain locations are *very* much greater than the field produced in the bulk by the interface charges. This, in turn, requires that the surface layers be sufficiently thin.

Thus it will be seen that this model has so far predicted, (i) the sign of the residual signal is the same, irrespective of the direction in which the crystal was poled at room temperature, and that the signal will be weaker if it has the same sign as that of the bulk virgin crystal at room temperature, (ii) that the sign of the residual signal is opposite to that of the bulk virgin crystal, and is the same irrespective of which side of the crystal is illuminated, and (iii) that the effect of applying a field above the Curie point is to produce a $\pm P_1$ type of polarization which will relax rapidly (normal dielectric relaxation) when the field is removed.

Pursuing this model it is natural to ascribe the annealing out of the residual signal to the gradual annihilation of the compensation charges around the old domain locations. (In practice, the signal-to-noise ratio for the residual signals was often much less than 10 and so the field due to the compensation charge would have to reduce by only an order of magnitude for its effect to become invisible.)

There remains the matter of the repolarizing direction. As the experiments showed that sometimes virtually the whole crystal polarizes in the same sense, it seems reasonable to invoke the remaining interface charges as the cause of this effect. The field produced by the interface charges throughout the bulk of the crystal may be small but quite sufficient to cause the whole crystal to repolarize in the same sense as it cools through the Curie point since the coercive field vanishes at the Curie point. Thus the model predicts that the crystal repolarizes in the direction of the field last applied to it, or, if a virgin crystal, in the direction in which the crystal was originally polarized. The opposite effect that occurs after a poling field has been applied for several hours can most likely be explained by a building up of an opposing space charge field due to carrier drift and it is conceivable that under certain configurations such a space charge field could over-rule the effects of the interface charges through the bulk of the crystal.

Thus the proposed model appears to be in satisfactory qualitative agreement with the experimental observations. It is therefore worthwhile to examine it more quantitatively. The qualitative argument requires that the pyroelectric signal due to P_1 be small relative to that caused by P_2 or P_3 and yet the field giving rise to P_1 must be sufficient to produce a strong preference for the appropriate polarizing direction when the crystal cools down. It was found that fields between 10^2 and 10^3 v cm⁻¹ had to be applied to the crystal above the Curie temperature to induce a pyroelectric signal comparable to the residual signal. Thus the field in the bulk of the crystal due to the remaining interface charge will normally be less than 10^2 v cm⁻¹. Since it has been found⁹ that at room temperature domains will grow under applied field strengths of less than 30 v cm⁻¹, it is reasonable to suppose that at the Curie point, a field ~ 1 v cm⁻¹ may be sufficient to determine the polarization direction of the crystal on cooling. We are thus able to put some limits on the width of the surface layer. Assuming a uniform dielectric constant, we have

$$10^2 > (4\pi\sigma/\epsilon)(2l/d) > 1 \text{ v cm}^{-1},$$

where σ is the interface charge density, l is the surface layer thickness, and d is the crystal thickness. Near the Curie point the dielectric constant, ϵ , is of the order of¹⁰

10^3 . Putting $d=10^{-2}$ cm we obtain,

$$10^{-1} > \sigma l > 10^{-3} \text{ esu.}$$

The maximum value that σ can have is $P_s \simeq 7 \times 10^3$ esu though its value will have decayed somewhat by the time the crystal is cooling through the Curie point. Thus a lower limit on l is $\sim 10^{-7}$ cm while its upper limit could be two or more orders of magnitude higher depending on how much σ had decayed and the value taken for the lower limit on the field. On the other hand, the thickness of the surface layers will be decreased if the dielectric constant, ϵ_l , in the surface layer is less than that of the bulk of the crystal. (To a first approximation, l is proportional to ϵ_l .) The maximum field *within* the surface layer (putting $l=10^{-7}$ cm and $\epsilon_l=10^3$) will be about 3×10^4 v cm⁻¹ near the Curie point and about 20 times greater at room temperature. Thus the thinnest estimate for the surface layer does not give rise to fields greater than what the breakdown strength of the crystal is likely to be. It is concluded, therefore, that these quantitative implications of the proposed model are compatible with it.

Finally, in view of the apparent success of the proposed model for explaining the residual signals and the repolarizing effects, it is worth examining the initial assumptions more closely.

(i) *Surface layer.* The existence of surface layers of various sorts in barium titanate crystals has been postulated by various authors^{11,12} and some experiments seem to demonstrate their existence. Surface layers can be classified into two broad types; (1) electric dipole layers as proposed originally by Känzig¹¹ and invoked by Chynoweth⁷ to explain residual pyroelectric signals and by Merz¹³ in an attempt to account for the thickness dependence of switching times in barium titanate, and (2) chemically or mechanically disturbed layers which take no part in the polarization reversal process but will give rise to interface charges, the effects of which on switching have been discussed recently by Drougard and Landauer.¹² It is this second type of layer which has been invoked in this paper. In triglycine sulfate crystals it is readily conceivable that such distorted layers occur at the crystal surfaces though to what depth is rather speculative. When examining a triglycine sulfate crystal under the microscope appreciable changes can be wrought in its topology by exposing it to high humidity (or by breathing on it). Also, when crystals are held at a temperature of 70°C or more for a few minutes, their surfaces become noticeably "sticky." Thus, the surface layers of these crystals cannot be regarded as good stable lattices and in fact, they may be quite amorphous. It is perfectly conceivable that similar damage occurs to the surface layers during the

¹¹ W. Känzig, Phys. Rev. **98**, 549 (1955).

¹² M. Drougard and R. Landauer, J. Appl. Phys. **30**, 1663 (1959).

¹³ W. J. Merz, J. Appl. Phys. **27**, 938 (1956).

¹⁰ S. Hoshino, T. Mitsui, F. Jona, and R. Pepinsky, Phys. Rev. **107**, 1255 (1957).

evaporation of the metallic electrodes and so the assumption of a surface layer which does not take part in the polarization reversal seems a very reasonable one for triglycine sulfate.

(ii) *Relaxation of compensation charge.* The model requires that the compensation charge that is left around the sites of the domains relaxes with a time constant $\approx 10^2$ sec for most crystals. This in turn requires the resistivity of the crystal to be of the order of 10^{12} ohm cm, which is very reasonable.¹⁴ (The relaxation time will decrease as the temperature moves away from the Curie point because of the falling dielectric constant).

(iii) *Existence of real or latent internal domains.* Figs. 10(a) and (b) provide positive proof that there exists in the crystal regions which are very strongly disposed toward a definite orientation of the polarization. However, there is no clue at this stage as to the causes of such regions, i.e., what kind (or kinds) of crystal imperfections or nonuniformities are responsible for them. It has not been ascertained yet whether these internal domains provide the internal nucleation sites that other experiments have indicated do exist.¹⁵

CONCLUSIONS

The spontaneous polarization as a function of temperature as deduced from the pyroelectric studies fits well the previously published data obtained directly over the temperature range where the two sets of data overlap. The spontaneous polarization increases more and more slowly as the temperature is lowered and there

is no indication of any phase transition down to -140°C . The validity of the dynamic pyroelectric technique is again established by these investigations.

The field-induced pyroelectric behavior above the Curie point shows departures at low fields from the behavior predicted by Devonshire's equation. There is qualitative agreement at higher fields but a transition temperature extrapolated from the higher field data is abnormally low. The causes of these discrepancies are not known with certainty but they may be connected with ferroelectrically inactive surface layers.

As in barium titanate, pyroelectric signals (at zero applied field) can still be generated above the Curie point. It seems that these can be accounted for in triglycine sulfate by the compensation fields which surround internal domains that have been shown to exist inside the crystal. These domains remain oriented in the same direction regardless of the polarization direction of the bulk of the crystal but the factors giving rise to these domains are not known. It is not known whether any of these remarks can apply also to barium titanate.

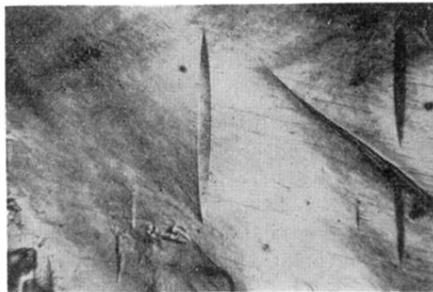
The marked tendency for a triglycine sulfate crystal to repolarize (on cooling through the Curie point) in the same direction in which it was previously poled is explained on the basis of the postulated existence of a surface layer which does not take part in polarization reversal processes and hence gives rise to interface charges.

ACKNOWLEDGMENT

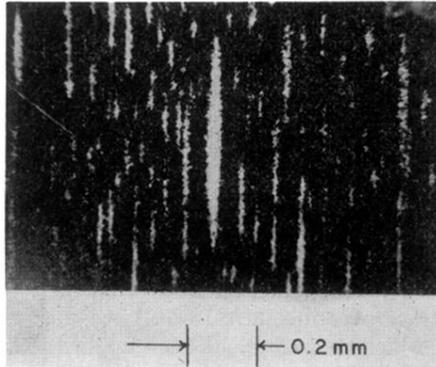
The author is indebted to W. L. Feldmann for his assistance with the domain delineations.

¹⁴ R. C. Miller, and C. D. Green (unpublished work).

¹⁵ A. G. Chynoweth and J. L. Abel, *J. Appl. Phys.* **30**, 1615 (1959).

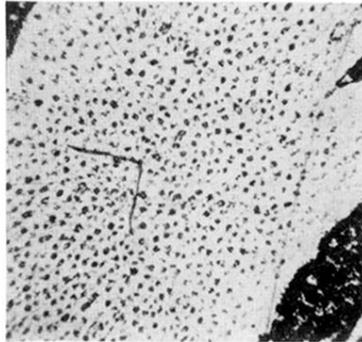


(a)

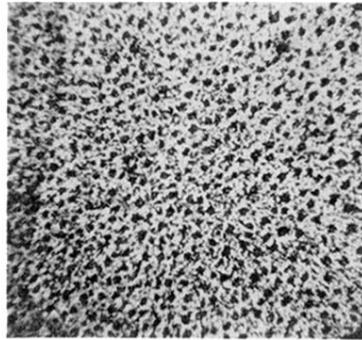


(b)

FIG. 10. Domain patterns on the side of the crystal *parallel* to the ferroelectric axis: (a) as revealed by a water etch, (b) as revealed by the powder method.



(a)



(b)

FIG. 9. Power deposition patterns showing fine domain detail in regions of basically uniform polarization. Figures (a) and (b) show two different parts of the same virgin cleavage slice, the two parts having basically opposite polarization directions. The fine detail is present in both regions.