# Radiation Damage Effects in Ferroelectric Triglycine Sulfate*

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Peculiar changes in the ferroelectric hysteresis loops of single crystals of triglycine sulfate result when the crystals are subjected to ionizing radiations (x-rays and electrons). Fully polarized crystals develop hysteresis loops biased along the field axis while partially polarized crystals develop double-loop patterns, each subsidiary loop being biased to the same extent but in opposite directions. The biased loops retain their rectangularity during the early stages of the bombardment. The bias field builds up steadily during the bombardment while the reversible polarization shows no change at first but eventually, at a fairly well-defined value of the bias field, it begins to decay in a fairly rapid manner.

Unusual field- and temperature-dependent changes in the shapes of the "damaged" hysteresis loops are observed. Under certain conditions, a double-loop pattern will "anneal" into a normal single loop simply as a result of applying the ac field; but when the field is removed, the crystal relaxes back to its double-loop form. Such cycles can be repeated, apparently indefinitely, provided that the field is not removed for too long a period. If this happens, the double-loop pattern fails to respond to further field treatments though it can be returned to the more unstable state by gentle heat treatment of the crystal.

The experiments rule out explanations of the effects based on the setting up of space charge fields or on nonuniform damaging of the crystal. It seems most likely that the effects are caused by the gradual building up of a more or less uniform strain in the crystal. The results are discussed in terms of the conventional double-minimum potential energy curve used for describing ferroelectric mechanisms. On the basis of some pyroelectric studies, however, it appears that a rather more complicated potential energy curve is needed to describe ferroelectricity in triglycine sulfate.

It is pointed out that, as the x-ray dosages required to produce large changes in the ferroelectric properties are small compared with those usually used in crystallographic structure determination, it seems most unlikely that the structure of an undamaged triglycine sulfate crystal has yet been determined, and one wonders how true this may be of certain other structure determinations for radiation-sensitive organic crystals.

## INTRODUCTION

WHILE studying the effects of radiation damage on the electrical properties of ferroelectrics, some strange results were obtained when triglycine sulfate crystals were subjected to ionizing radiations. In some preliminary experiments electrons of up to 1-Mev energy from a Van de Graaff accelerator were used, and it was found that even at electron beam current densities of a few microamperes per square centimeter the ferroelectric characteristics of the crystals deteriorated considerably in a few seconds. Furthermore, electrons of less than 100-kev energy also produced rapid deterioration of the dielectric hysteresis loop. Such low-energy electrons were unsuitable for controlled radiation damage experiments because of their low penetration into the crystal compared with the thickness of the crystal, thereby resulting in considerable nonuniformity in the amount of damage and, consequently, inhomogeneous strains in the crystal. To minimize this difficulty, all subsequent experiments were made using x-rays of up to 30-kev energy from an x-ray tube designed for x-ray diffraction work. The primary action of the x-rays is to liberate photoelectrons more or less uniformly throughout the volume of the crystal and with energies ranging up to the maximum photon energies present. This paper describes the effects such radiation has on the conventional dielectric hysteresis loop and on the pyroelectric properties of the crystal. The ferroelectric mechanism of a crystal is usually pictured with the aid of a potential energy diagram, generally the well-known double-minimum curve. To account for the radiation damage effects in triglycine sulfate it seems necessary to modify this idealized curve somewhat and to ascribe certain progressive changes to it during the bombardment.

## EXPERIMENTAL

Ferroelectricity in triglycine sulfate crystals was reported by Matthias, Miller, and Remeika.[1] The crystals used in these experiments, which were grown by Remeika, were cleaved into thin slices. These slices were ground down to the desired thickness, usually about 0.005 inch. Crystals of this thickness produced only a few percent attenuation of the x-rays. Early in these investigations it became obvious that many of the strangely distorted hysteresis loops observed with freshly prepared samples could be traced to the use of x-rays to determine the crystallographic orientations in the parent crystal preparatory to cleaving or cutting. All the results described here were obtained using crystals that had not previously been exposed to x-rays at any time; as the cleavage plane is perpendicular to the ferroelectric axis it was not essential to use x-rays to determine the crystallographic orientation.

The thin crystal slices were cut into units about 3 mm square and gold electrodes, 2 mm in diameter, were evaporated opposite each other on the major faces. The leads were narrow strips of aluminum foil, affixed to the gold electrodes by minute spots of air-drying silver paste. The other ends of the leads were cemented onto a microscope slide using silver paste.

The crystal was mounted about 1 cm from the window of the x-ray tube where it was subjected to the

* This work was supported in part by the Wright Air Development Center of the U. S. Air Force.

[1] Matthias, Miller, and Remeika, Phys. Rev. 104, 849 (1956).

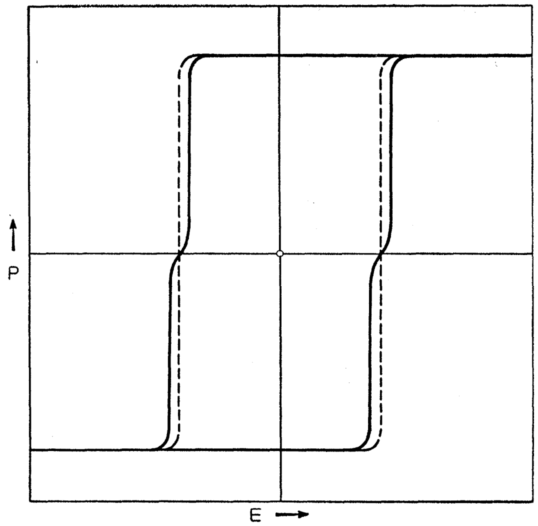



FIG. 1. Transient change in the shape of the hysteresis loop as frequently observed in crystals subjected to an electric field for the first time. The solid line represents the initial shape of the loop.

full spectrum emitted by a copper target. Except where noted otherwise, the electrical measurements were made with the x-rays turned off. Many of the hysteresis loop measurements were made using the well-known Sawyer-Tower circuit. However, this has phase compensation controls the settings of which are rather arbitrary, making measurement of the coercive force unreliable. This difficulty is avoided with a second type of circuit which was used in all the later work, the circuit having been developed by Diamant, Drenck, and Pepinsky.[2] The loops were normally obtained using the line frequency of 60 cps. The pyroelectric measurements were made using the light-chopper technique that has been described previously.[3]

## RESULTS

### (a) Hysteresis Loops of Undamaged Crystals

In practice it was usual to increase gradually from zero the amplitude of the ac field applied to the crystal, thus enabling the onset of the hysteresis loop to be

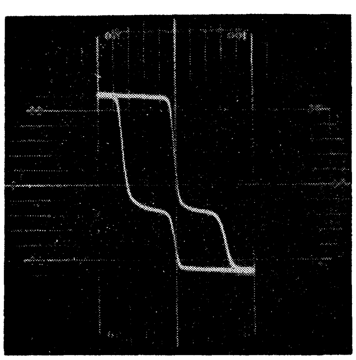


FIG. 2. Typical distortion of hysteresis loop that results when triglycine sulfate crystals are subjected to "moderate" amounts of bombardment by x-rays.

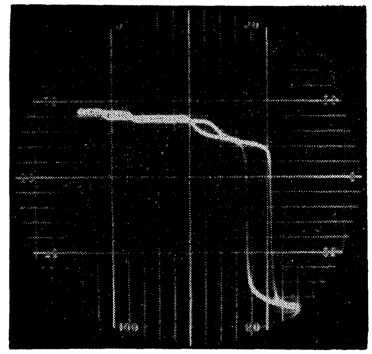
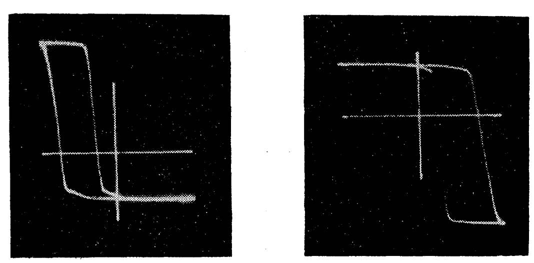


FIG. 3. Example of the more complex distorted hysteresis loops occasionally produced by x-ray bombardment.

observed on the oscilloscope. Crystals subjected to switching fields for the first time usually exhibited peculiar little kinks in their hysteresis loops at approximately zero polarization, the kinks being particularly noticeable when the maximum amplitude of the field was just sufficient to switch a major fraction of the crystal. These kinks, which are shown in Fig. 1, always died out within a few seconds whereupon the loop became normal and almost rectangular. The kinks could not be made to reappear by removing the field temporarily.

### (b) Changes Observed in Shapes of Hysteresis Loops during Bombardment

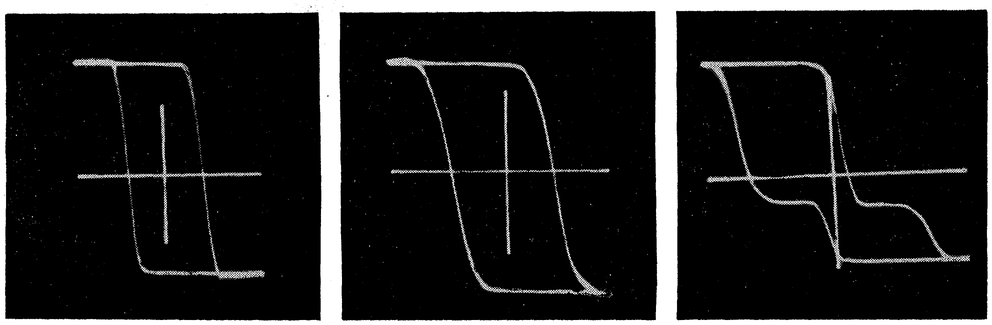
The first experiments were with unpoled crystals (i.e., less-than-saturated polarizations). After moderate bombardment the hysteresis loops take on forms of which Fig. 2 is a typical example. The striking feature is that the original rectangular hysteresis loop has split up into two separate loops, each fairly rectangular, and which are biased by equal and opposite amounts along the field axis. The heights of the two loops are usually different but their sum is equal to the height of the loop before damaging. As the bombardment continues, the separate loops retain their individual heights but the bias field increases steadily so that the two loops move further and further apart. (The bias field is defined as the value of the applied field corresponding to the center of the hysteresis loop.) Sometimes more complex hysteresis patterns were



(a) (b)

FIG. 4. Biasing effects produced in two similar crystals subjected to identical bombardments, the crystals having been polarized to saturation before the bombardment by dc fields of opposite polarities.

[2] Diamant, Drenck, and Pepinsky, Rev. Sci. Instr. **28**, 30 (1957).
[3] A. G. Chynoweth, J. Appl. Phys. **27**, 78 (1956).



(a) (b) (c)

FIG. 5. Effect of maintaining an ac field on the crystal during the bombardment: hysteresis loops (a) before the bombardment, (b) at the end of the bombardment, and (c) after removing the field for a few minutes.

observed suggesting three, or even four, loops altogether. An example of this is shown in Fig. 3.

A pattern for the major biasing effects was established as follows. If, before the bombardment, the crystal was polarized to saturation by a short application of a dc field, the bias developed as before but the loop moved as a whole rather than splitting up into two loops. This is shown in Fig. 4. Furthermore, the direction in which the loop biased depended on the direction of the dc field used for the initial polarizing of the crystal. The pyroelectric measurements to be described later showed that if the crystal was polarized with a negative field the loop developed a bias in the positive field direction, and vice versa.

Next, a 60-cps field of amplitude considerably greater than the coercive field was applied throughout the bombardment. During the bombardment the appearance of the hysteresis loop remained normal apart from a relatively slight increase in the coercive field [Fig. 5(b)]. However, if the field was removed for several minutes and then reapplied, the loop showed a splitting, as shown in Fig. 5(c). More of these time effects will be described later but this experiment again indicates that the sign of the bias developed by the crystal, or individual domains thereof, depends only on the direction of the spontaneous polarization in the crystal, or individual domains. Furthermore, the fact that the separating loops remain fairly rectangular shows that the magnitude of the effect brought about by the bombardment is the same in every part of the crystal. Also, the clean separation of the loops shows that the damaging effects in a part of the crystal polarized in one direction proceed independently of what is happening in an adjacent region polarized in the opposite direction.

### (c) Effect of Bombardment of Crystal above the Curie Temperature

A crystal, whose initially normal room-temperature hysteresis loop is shown in Fig. 6(a), was subjected to the 30-kv radiation while it was kept at a temperature considerably higher than its Curie point. No field was applied during this bombardment which lasted for 10 minutes, a period sufficient to make the biasing effects apparent. At the end of the bombardment the crystal was cooled to room temperature whereupon its hysteresis loop [Fig. 6(b)] at first appeared rather like the split loop of Fig. 5(c). However, maintaining the ac field for a few minutes caused the loop to return to normal [Fig. 6(c)]. If the field was next removed for several minutes and then reapplied, the hysteresis loop initially appeared split [Fig. 6(d)], but again, the normal loop was soon regained if the field was maintained.

### (d) Effect of Energy of X-Rays

For most of the experiments the x-ray machine was run at 30–35 kv, producing the behavior described above. However, very similar results were obtained with the machine running at 8 kv, although, on account of the reduced intensity, the bombardment times had to be considerably greater to produce comparable effects. In one experiment a crystal was exposed for several hours to the radiation from the machine running at 3 kv and there were indications that the same sort of loop splitting and biasing effects were occurring. Thus there appears to be no appreciable threshold

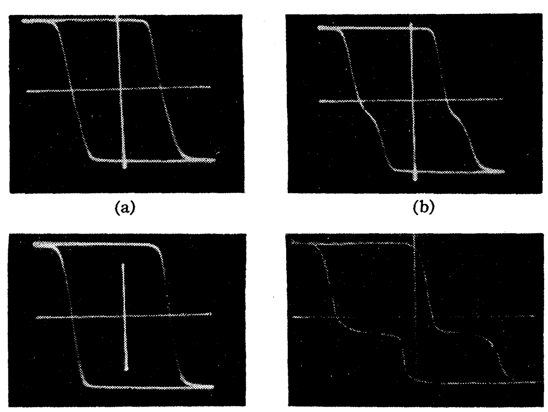


FIG. 6. Effect of maintaining the crystal above its Curie temperature during the bombardment: hysteresis loops (a) before the bombardment, (b) immediately after cooling the crystal at the end of the bombardment, (c) after keeping the ac field on the crystal for a few minutes, and (d) after removing the field for a few minutes.

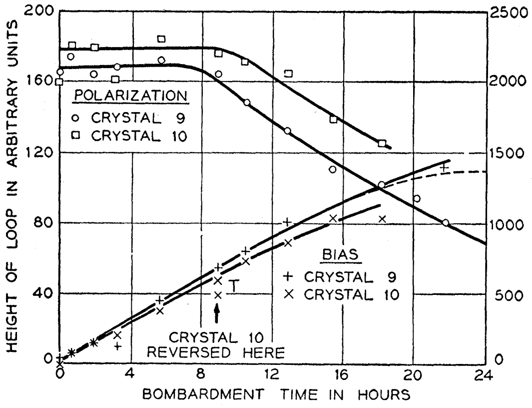



FIG. 7. Variation of the bias field and the spontaneous polarization during the bombardment with 8-kv x-rays.

energy required of the x-rays in order to produce the effects, suggesting that the damage results from the effects of ionization rather than from ionic displacements. With the maximum energy transfer possible, a 3-kv electron could just displace a hydrogen atom if its displacement energy were not more than about 8 ev.

### (e) Bias Field *vs* Bombardment Time

Figures 7 and 8 show the changes in the bias field with bombarding time with the x-ray tube running at 8 kv, 15 ma, and 30 kv, 20 ma, respectively. The three crystals used in these measurements all had thicknesses of about 0.005 inch and had similar hysteresis loops to start with. They were not polarized prior to the bombardment and so they developed split loop patterns. The bias fields plotted in Figs. 7 and 8 refer in each case to the average of the magnitudes of the bias fields developed by the subsidiary loops. It will be noted that the bias field increases more or less linearly with time though it is difficult to establish the behavior after long bombardments as the quality of the loop is then deteriorating rapidly. Referring to Fig. 7, the x-rays were incident on the same face of crystal 9 throughout the bombardment while crystal 10 was turned over at the point $T$, about half-way through the bombardment, so that the x-rays were thereafter incident on the face opposite the one bombarded initially. It will be noted that turning the crystal over had no apparent effect on the progress of the bias field during the bombardment.

It was also determined that the biasing effect was not changed in any way if the crystal was shorted during the bombardment.

In Fig. 9 the bias field *versus* bombardment time is shown for two different crystal thicknesses and it is apparent that the bias field produced by the bombardment is independent of the crystal thickness to within experimental error.

### (f) Spontaneous Polarization *vs* Bombardment Time

Also shown in Figs. 7 and 8 is the way the spontaneous polarizations, $P_S$, are affected by the bombardment. For a quite well-defined period there is no noticeable change in $P_S$ but at the end of this period a relatively rapid decay begins and with continuing bombardment, the decay is quite abrupt rather than a gradual tailing-off. It is interesting to note that the breakover in $P_S$ occurs at the same value of the bias field for all three crystals, to within experimental error. Further studies showed this result to be very reproducible among crystals of different thicknesses. The shape of the hysteresis loop remains quite rectangular during the period $P_S$ is constant but as $P_S$ decays the quality of the loop deteriorates; it becomes smeared out and resembles, somewhat, the loop shapes usually associated with ceramic ferroelectric materials.

### (g) Coercive Field *vs* Bombardment Time

Figure 10 shows the way in which the coercive field depends on the bombardment time, the coercive field being defined as half the width of the hysteresis loop whatever the value of the bias field. (For these measurements the ac field was maintained throughout the

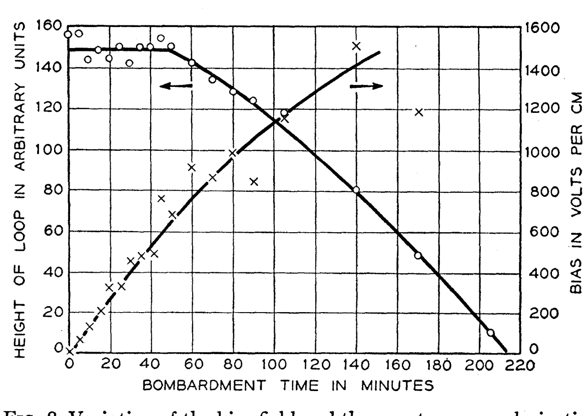



FIG. 8. Variation of the bias field and the spontaneous polarization during the bombardment with 30-kv x-rays.

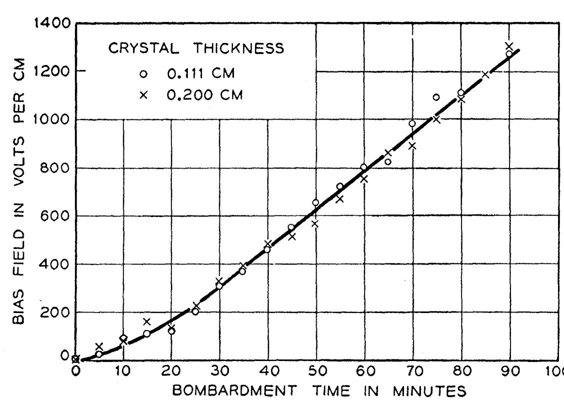



FIG. 9. Growth of the bias field with bombardment time for two crystals of different thicknesses.

bombardment.) The coercive field at first increases steadily during the bombardment to a maximum value, after which it goes into a steady decline. The maximum coincides, approximately, with the point at which the polarization starts to decrease.

### (h) Pyroelectric Measurements

After first examining its hysteresis loop, a crystal was polarized to saturation with a dc field and then subjected to a bombardment sufficient to reduce the spontaneous polarization by about 50%. At the completion of the bombardment the diminution in height of the hysteresis loop was checked. Pyroelectric measurements at zero applied field were made throughout the bombardment and it was found that both the magnitude and sign of the pyroelectric signal remained unchanged to within experimental error. From the fact that the sign did not change it was possible to deduce the direction of the biasing effect, as mentioned earlier. When a dc field sufficient to overcome the bias field and switch the crystal was applied, the pyroelectric signal reversed its sign but its magnitude showed no appreciable change. This result, at first sight, appears to contradict the hysteresis loop measurements but it should be remembered that the pyroelectric signal is determined primarily by $(dP/dT)$, the pyroelectric coefficient, which does not necessarily depend on the amount of *reversible* polarization.

### (i) Hysteresis Loop as a Function of Frequency

Another possible reason for the difference between the pyroelectric and hysteresis measurements is that the former are made under dc field conditions while for the latter, the field is alternating with a frequency of 60 cps. A decrease in the height of the hysteresis loop could conceivably be produced by dispersive effects becoming effective if the relaxation time for switching gets greater than or equal to the frequency. However, no difficulty was experienced in saturating the hysteresis

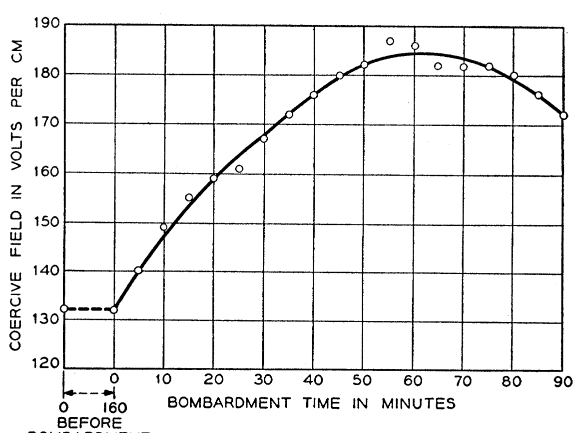



FIG. 10. Variation in the coercive field during the bombardment.

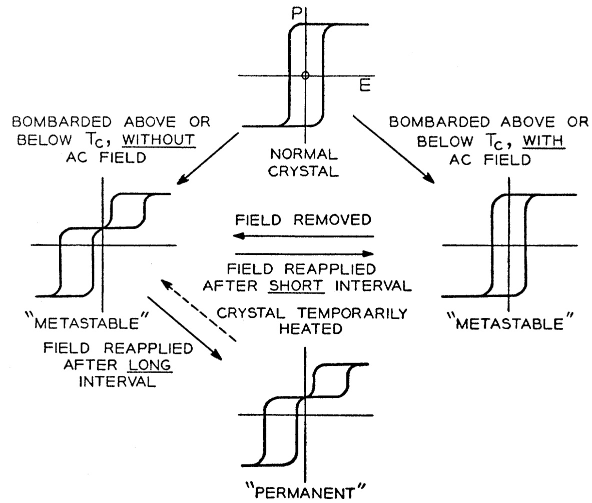



FIG. 11. Diagram showing the pattern of the bombardment and "annealing" effects.

loops; increasing the amplitude of the alternating field did not increase the height of the loop. Furthermore, the height of the hysteresis loop did not change over the frequency range from 15 cps to 1000 cps. Thus, dispersive effects appear to be ruled out.

### (j) Reversible Annealing Effects

Mention has already been made of time-dependent phenomena and to these will be added some further observations. Figure 11 shows, schematically, the behavior pattern of these effects. (The remarks in this section refer, primarily, to crystals that have been subjected to relatively short bombardment times, say 10 to 15 minutes.)

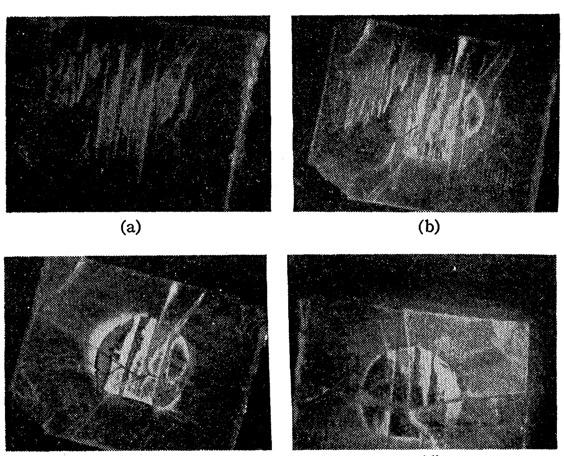
Starting with a randomly polarized crystal that shows a normal hysteresis loop, the split-loop hysteresis pattern is revealed when the field is applied immediately after the bombardment, the latter having been carried out either above or below the Curie point but without an applied field. However, as the field is maintained, the two parts of the loop "slide" towards each other along the field axis and eventually merge to form a normal hysteresis loop, though with slightly greater coercive field than initially. This "annealing" takes place in a time of the order of a minute. If the field is then removed for about a minute the split loop pattern is again obtained when the field is reapplied. Alternatively, if the field is maintained throughout the bombardment, with the crystal either above or below the Curie point, there is no splitting observable at the end of the bombardment. But again, briefly removing the field enables the crystal to adopt a split-loop pattern which also anneals back to a single loop as the field is maintained. The process of relaxing to a split-loop pattern with the field off and its subsequent annealing with the field on could be repeated continuously provided that the field was not removed for too long a period, say half an hour or more.

If the field was removed for too long, the split-loop pattern became permanent, the field no longer having the annealing effect. However, if the crystal was heated to about 80°C for a few seconds (with a heat lamp) and then cooled rapidly to around room temperature, it returned to its previous unstable state where it could be cycled by the field between the split- and single-loop patterns. It was established that it was not sufficient merely to heat the crystal to above its Curie point momentarily. It was also found that dc fields annealed out the split-loop pattern in a way similar to that of the ac field.

The above remarks apply in particular to crystals that had been damaged only slightly, that is, by an amount much less than that required to make $P_S$ decrease. However, qualitatively similar behavior was observed in severely damaged crystals where $P_S$ had dropped by more than 60%. Heating the crystal to about 140°C for 30 minutes caused the loop to return to its normal height and the bias field to become zero. The fact that the annealing took some time at 140°C shows again that it is not sufficient merely to take the crystal momentarily to a temperature greater than its Curie point. In no instance has it proved possible to permanently anneal out the effects of the bombardment with gentle heat treatments of the sort described above.

### (k) Positive Evidence of Clamped Domains

From the preceding section it is evident that the crystal has a memory for the effects of the radiation and that this memory is not obliterated by field or heat treatments. In particular, the loop of a partially polarized crystal splits up during the bombardment into two loops, the relative sizes of which depend on the relative amounts of polarization in the two directions initially. Even after heat treatment, the split-loop pattern usually returns with the loop sizes in about the same ratio as previously. This suggests that the original domain pattern must be regained. This conclusion was confirmed by using the beautiful powder deposition techniques that have been developed by Pearson and Feldmann.[4] In these, a drop of hexane containing a fine suspension of lead oxide or sulfur powder is placed on the surface of the crystal and, as the hexane evaporates, the powder settles preferentially where domains of a particular polarization direction intersect the surface. The powder deposition pattern obtained on the surface of a slab of a triglycine sulfate crystal prior to bombardment is shown in Fig. 12(a). The powder was then cleaned off and a circular area near the center of the crystal bombarded for about 1 hour with the 30-kv radiation. The powder pattern obtained after this bombardment is shown in Fig. 12(b). It will be seen that the domain pattern is essentially the same both inside and outside the bombarded area. However, it was noticed that the powder had a preference for settling on the bombarded area rather than the unbombarded area, probably caused by charging of the crystal during the bombardment. This was particularly noticeable for domains which extended across the boundary of the bombarded area, several examples being obvious in Fig. 12(b). Next, after again cleaning the crystal, it was heated to around 80°C for about a minute. When it had cooled to room temperature a fresh powder pattern was obtained; this is shown in Fig. 12(c). It is obvious that the domain pattern outside the bombarded area has been considerably modified and in fact it gives the appearance of having become almost a single domain. On the other hand, the bombarded area has re-established at least the main features of the original domain pattern. The other side of the crystal, which was about 2 mm thick, gave a powder pattern which was essentially the mirror image of that on the bombarded face, showing that the domains extended right through the crystal. From these experiments it is concluded that as a result of the radiation-produced damage a region of the crystal originally occupied by a particular domain strongly encourages the reformation of that same domain after heat treatment (and, presumably, after field treatment).




(c) (d)

FIG. 12. Domain structures as revealed by the powder pattern technique: (a) before bombardment, (b) after bombarding a circular region in the center of the crystal, (c) after heating the crystal to above the Curie point for a few minutes, and (d) the opposite side to that of (c).

### (l) Evidence for Severe Strain in Crystal

After appreciable bombardment of thick samples it was found that they cracked very easily, often with relatively gentle handling. This indicates that the bombardment results in considerable strain in the crystals.

[4] G. L. Pearson and W. L. Feldmann (to be published).

### (m) Estimate of Radiation Dosage

Rough estimates were made of the radiation dose required to deteriorate the hysteresis loops to about one-half of their original height. For both electron and x-ray bombardments this dose could be expressed as equivalent to an energy expenditure of about 10 ev per unit cell. This estimate could be out by an order of magnitude either way but it is certainly compatible with the damaging-by-ionization mechanism.

## DISCUSSION

As described above, it seems fairly certain that the main damage-producing mechanism is not by atomic displacements but by ionization followed by chemical reactions resulting in molecular rearrangements. Radicals formed as a result of the ionization could be relatively stable when confined within the crystal lattice. However, the behavior of the hysteresis loops cannot be explained directly by the properties of the gradually accumulating damaged unit cells since the whole crystal has to reflect a relatively minor amount of local damaging if the hysteresis loop is to retain its entity throughout the initial stages of the bombardment. In particular, the results cannot be explained by the steady accumulation of randomly located damaged cells or regions in which, for example, (i) the spontaneour polarization has been changed in magnitude, or made zero, or changed in direction, (ii) the coercive force has been changed by a discrete amount, (iii) the dielectric permittivity has changed, or (iv) a conversion to antiferroelectric behavior has been produced.

Another possibility is a multiple-hit process which would require the damaging of several adjacent cells in order to destroy the dipole coupling across the damaged portion, or the creation of two damaged regions along a dipole chain so as to inhibit the switching of the dipole chain between them. Such a model could possibly fit the variation of the spontaneous polarization with time but it would not account readily for the biasing effects.

Conceivably, local damaging could indirectly affect the whole crystal through the creation of over-all space charge fields or elastic strain. The first, as a possible explanation of the biasing, is ruled out for several reasons. In particular, the space charge fields would have to be microscopically detailed with the fields acting on each domain in the direction appropriate to its polarization, while the results of the bombardment above the Curie point go further; they suggest that on cooling down, each unit cell would have to have its own hypothetical space charge field of appropriate sign, a clearly absurd situation. Also, the absence of any noticeable change in the growth of the bias field with bombardment time when the crystal is turned over is contrary to what one would expect if an over-all space-charge field were being built up. These conclusions are further supported by the fact that there was no noticeable change in the damaging effects if the crystal was shorted during the bombardment. These arguments would seem to apply to any arbitrary space charge distribution. The building up of strain is a more attractive hypothesis and the cracking of crystals is a sure sign of strain though, to date, attempts to measure changes in the lattice constant during the bombardment have been unsuccessful. However, the failure of the biasing effect to reverse direction when the crystal is turned over shows that the effects are not due simply to the building up of a nonuniform strain.

Not knowing the detailed origin of the radiation damage effects and not knowing very much about the crystallographic structure and the ferroelectric mechanism in triglycine sulfate, about all that can be done at this stage is to discuss them in terms of a phenomenological model based on a potential energy diagram. It will be supposed that the steady accumulation of damage is reflected in a steady change in the shape of the double-minimum potential energy curve usually used for describing ferroelectric mechanisms. This progressive change may come about through the agency of uniform strain which could be the case in a two-phase crystal regarding the damaged and undamaged regions as the two phases. A progressive change which fits most of the experimental facts is shown in Fig. 13. It is not intended that this is the true explanation for the effects, but merely to show that it is possible to arrive at *some* such model which accounts for them. The ion responsible for the ferroelectric mechanism has either of the two potential minima, $A$ and $B$, available to it in the undamaged state. It will be supposed that the effect of the radiation is to modify one side of the energy diagram with respect to the other and in particular, it will be supposed that the minimum in which the ion happens to reside is *relatively* unaffected by the radiation. In this way one can account for the dependence of the sign of the bias field on the initial polarization direction. If, during the bombardment, minimum $B$ is steadily raised relative to that at $A$ one can account for the bias field which is equivalent to a tilt of the undamaged energy curve. Maintaining constant, at first, the horizontal distance between the

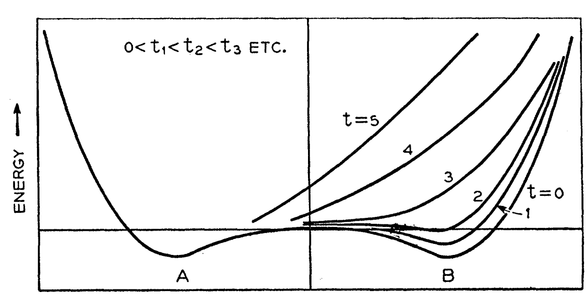



FIG. 13. Hypothetical phenomenological model that accounts for the major changes in the ferroelectric properties with increasing bombardment time, *t*.

two minima can account for the initial constancy of $P_S$. If minimum $B$ is gradually obliterated the crystal will become polar and nonferroelectric, as confirmed by the persistence of the pyroelectric effect after the hysteresis loop has been considerably deteriorated. However, this model would not account for the reversibility of the undiminished pyroelectric signal in the heavily damaged crystal though with sufficient ingenuity, such as by adding finer structure to the energy curve and making further assumptions, one could account for this also. Nevertheless, it would seem that simple changes in a simple double-minimum potential curve cannot account for all the experimental facts and a more complicated curve is required. This is equivalent to adding more terms to the usual expression for the free energy as a function of crystal polarization but such an analysis is unlikely to be profitable until more is known about the nature of the ferroelectric mechanism in triglycine sulfate.

Little can be said at present about the peculiar annealing effects and time-independent changes in the hysteresis loops though it is of some interest that somewhat similar results have recently been observed in $(Pb_\lambda Ca_{1-\lambda})TiO_3$ ceramics by Sawaguchi, Mitsuma, and Ishii,[5] in mixed single crystals of $(K_\lambda Na_{1-\lambda})NbO_3$ by Cross,[6] and in $BaTiO_3$ crystals with various deliberately added impurities.[7] Cross has indicated that at least some of his results can be explained in terms of a thermodynamic treatment of the properties of solid solutions that he has given previously.[8]

Mitsui[9] has suggested that the radiation damage effects might be ascribed to a migration of the imperfections produced by the x-rays into the domain walls. This process is quite feasible as there is probably a strong mechanical stress field within or near a domain wall, as discussed by Mitsui and Furuichi,[10] which will provide favorable sites for some crystal imperfections. Imperfections segregating in this way could serve to trap the domain wall. Such a mechanism appears attractive in that one could more readily account for the memory effects and possibly the time effects also. However, the experiments have shown that the presence of domain walls is not necessary for the production of biased hysteresis loops or a decrease in the polarization, and the author feels that it would be too speculative to pursue this model further until more experimental studies have been made.

Finally, it should be noted that as the x-ray dosages required to produce large changes in the ferroelectric properties are small compared with those usually used in crystallographic structure determinations, it would seem most unlikely that the structure of an undamaged triglycine sulfate crystal has yet been determined by x-ray crystallography. One wonders, also, how true this may be of certain other structure determinations for radiation-sensitive organic crystals.

[After this paper was written, the author found that strikingly similar behavior has been observed in Rochelle salt crystals damaged by nuclear radiation or x-rays. Zheludev and Iurin[11] observed splitting of the hysteresis loop when the crystals were bombarded with $\gamma$ and x-rays. Very similar split-loop patterns were also observed by Eisner[12] in Rochelle salt crystals that had been doped with boron or copper during growth. It therefore seems that split hysteresis loops occur quite generally in distorted ferroelectric crystals, and they may be explicable in terms of some thermodynamic theory.]

[5] Sawaguchi, Mitsuma, and Ishii, J. Phys. Soc. Japan **11**, 1298 (1956).
[6] L. E. Cross, Nature **181**, 178 (1958).
[7] J. P. Remeika and G. W. Brady (private communication).
[8] L. E. Cross, Phil. Mag. **1**, 76 (1956).
[9] T. Mitsui (private communication).
[10] T. Mitsui and J. Furuichi, Phys. Rev. **90**, 193 (1953).
[11] I. S. Zheludev and V. A. Iurin, Bull. Acad. Sci. U.S.S.R. English translation **20**, 193 (1956), and Bull. Acad. Sci. U.S.S.R. English translation **21**, 336 (1957).
[12] I. Ia. Eisner, Bull. Acad. Sci. U.S.S.R. English translation **21**, 341 (1957).

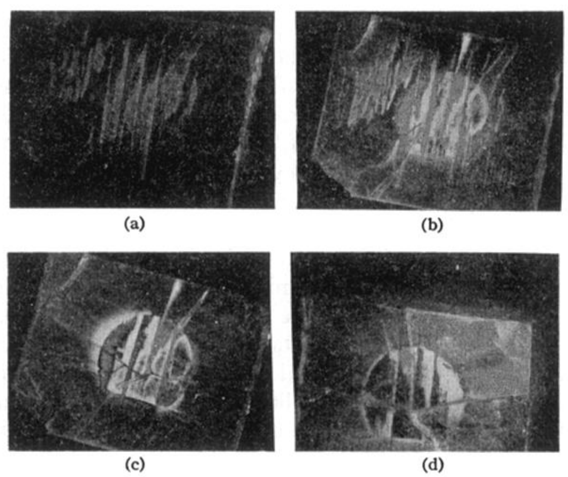



FIG. 12. Domain structures as revealed by the powder pattern technique: (a) before bombardment, (b) after bombarding a circular region in the center of the crystal, (c) after heating the crystal to above the Curie point for a few minutes, and (d) the opposite side to that of (c).

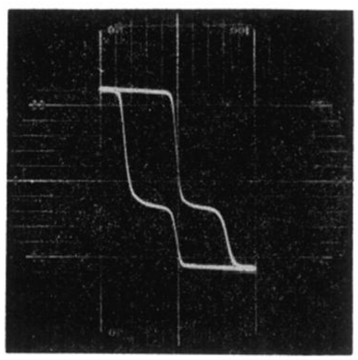


FIG. 2. Typical distortion of hysteresis loop that results when triglycine sulfate crystals are subjected to "moderate" amounts of bombardment by x-rays.

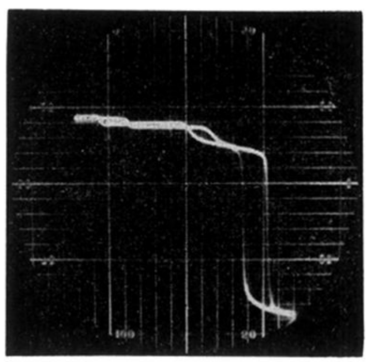
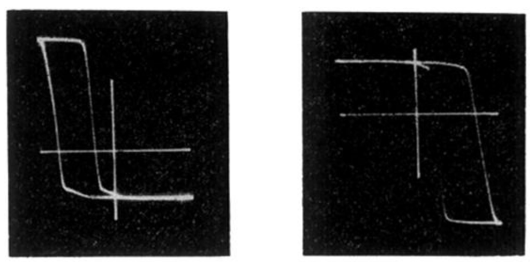


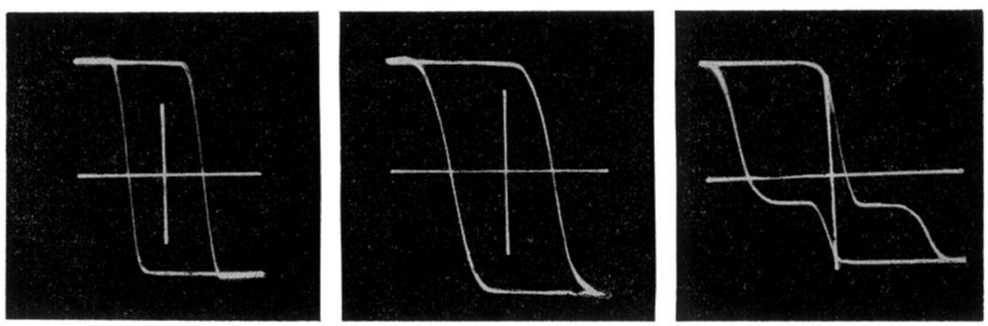
FIG. 3. Example of the more complex distorted hysteresis loops occasionally produced by x-ray bombardment.



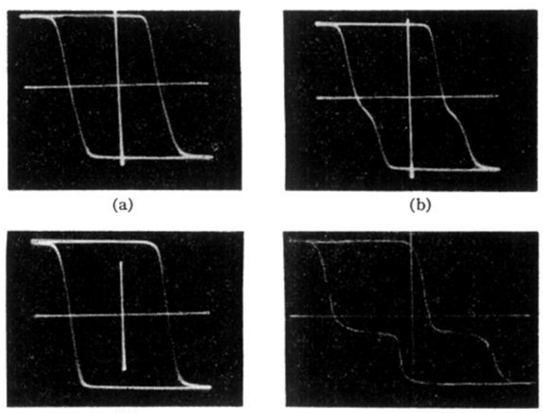
(a) (b)

FIG. 4. Biasing effects produced in two similar crystals subjected to identical bombardments, the crystals having been polarized to saturation before the bombardment by dc fields of opposite polarities.

Fig. 5. Effect of maintaining an ac field on the crystal during the bombardment: hysteresis loops (a) before the bombardment, (b) at the end of the bombardment, and (c) after removing the field for a few minutes.



(a) (b) (c)



(a) (b) (c) (d)

FIG. 6. Effect of maintaining the crystal above its Curie temperature during the bombardment: hysteresis loops (a) before the bombardment, (b) immediately after cooling the crystal at the end of the bombardment, (c) after keeping the ac field on the crystal for a few minutes, and (d) after removing the field for a few minutes.