Nuclear-Magnetic-Resonance Studies of Ferroelectricity in Normal and Irradiated Rochelle Salt*

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The ferroelectric properties of Rochelle salt have been studied by means of two new techniques based on the Na^{23} NMR. In the first technique, the separation between a pair of Na^{23} quadrupolar satellites is used as a measure of the spontaneous polarization of the crystal. Using this method, the effects of electric fields and γ irradiation on the polarization have been studied. The irradiation caused the spontaneous polarization to decrease in magnitude, but to persist over a wider temperature range than in an unirradiated crystal. In the second technique, a pair of quadrupolar satellites was identified as arising from oppositely polarized domains. The relative intensities of these satellites provides a measure of the fraction of the crystal polarized in the forward and reverse directions. Under the influence of an applied electric field, the relative intensities of the two satellites change. By studying these changes versus applied electric field, "quasistatic" hysteresis loops have been obtained which have a very low coercive field (25 V/cm). When the crystal is irradiated with γ rays, these hysteresis loops split into double loops. Finally, domain dynamics were studied by measuring the relative intensities of these satellites versus time after an electric field had been switched. The time required for polarization reversal was observed to depend on the magnitude of the applied electric field.

I. INTRODUCTION

NUCLEAR-MAGNETIC-RESONANCE (NMR) techniques have been used on several occasions[1–3] to investigate single-crystal Rochelle salt [NaK(tartrate)·$4H_2O$]. These studies were primarily concerned with elucidating the microscopic structure of this crystal in hopes of explaining the atomic origins of ferroelectricity.

In this paper it is shown how the quadrupole splitting of the Na^{23} ($I=\frac{3}{2}$) NMR can also be utilized to investigate spontaneous polarization, coercive field, and domain characteristics in the ferroelectric phase of Rochelle salt. Furthermore, the effects of ionizing radiation on these properties are studied with the aid of this new technique.

The spontaneous polarization and coercive field have already been extensively investigated as functions of temperature.[4–6] In most cases they were measured directly from hysteresis loops obtained with a Sawyer-Tower type bridge.[7]

Rochelle salt is structurally very complex.[8–11] Nevertheless, its domain structure is relatively simple, consisting of parallel and antiparallel polarized domains[12] and thus having only 180° domain walls. The domain structure has been inferred by many indirect methods.[13–15] Mitsui and Furuchi[12] first reported direct visual observation of domains by means of polarizing methods. The study of domain configurations and domain dynamics is important for the understanding of the processes involved in polarization reversal.

The polar phase of Rochelle salt is also known to be extremely sensitive to structural changes brought about by either radiation damage[16–23] or by substitutional[24] or nonsubstitutional impurities.[17]

Extensive investigation of electrical[16–23] as well as mechanical[25] properties of γ- and x-ray damaged

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Rochelle salt have been carried out over the past 10 yr. In every case the standard experimental techniques mentioned above were used. More recently, an ESR investigation[26] had identified some of the damage centers produced by x radiation. A slow-neutron spectroscopic study[27] has shown that the intensity of a reflection, characteristic of deuterated Rochelle salt in the polar phase, decreases as the accumulated damage increases, indicating that the polarization decreases. Optical-domain studies of damaged crystals, on the other hand, show that the polar phase is extended above the transition temperatures of the virgin crystal.

The experimental results are discussed in Sec. III and are divided into two main subsections. Section III A is devoted to the study of spontaneous polarization and Sec. III B to domain characteristics.

It is shown in Sec. III A 1 that the separation (in frequency) between a pair of Na^{23} satellite lines in the polar phase is proportional to the polarization. In Sec. III A 2 the effects of externally applied electric fields are considered. The effect of γ radiation on the polar phase and the results of applying external electric fields to damaged crystals are discussed in Sec. III A 3. In Sec. III A 4 it is shown that there are long-term aftereffects of radiation damage.

For a slightly different orientation of the single crystal with respect to the externally applied magnetic field each satellite line in the polar phase is observed to split into a pair of satellites of equal amplitude. This is attributed to parallel and antiparallel polarized domains in Sec. III B 1. The NMR observation of domains is then exploited to obtain quasistatic hysteresis loops in Rochelle salt in Sec. III B 2. In Sec. III B 3 a dynamic polarization switching experiment using NMR is described, and the effect of radiation damage on quasistatic hysteresis loops is described in Sec. III B 4.

II. EXPERIMENTAL TECHNIQUES

A. Crystal Orientation and the Na^{23} NMR Satellite Line Spectrum

In this section an explanation is given of the multiplicity of the Na^{23} satellite lines in the nonpolar ($T>+24$°C) phase as well as in the ferroelectric phase (-18°C$<T<24$°C).

Figure 1 shows a simplified unit cell of Rochelle salt containing four sodium atoms which are physically inequivalent.[1,2] The Na^{23} NMR spectrum is perturbed by a quadrupole interaction.[1,2] In the higher temperature nonpolar phase, for an *arbitrary orientation* of the crystal with respect to the externally applied magnetic field H_0, the spectrum consists of four upper satellites, ($m=-\frac{3}{2}\rightarrow-\frac{1}{2}$), four lower satellites ($m=+\frac{1}{2}\rightarrow\frac{3}{2}$), and four central lines ($m=-\frac{1}{2}\rightarrow+\frac{1}{2}$) shifted with respect to the Larmor frequency. The crystal symmetry of Rochelle salt above $+24$°C is orthorhombic $P2_12_12$, implying that there are twofold screw axes about X and Y directions and a twofold rotation axis about the Z direction.[8] These symmetry axes are also shown in Fig. 1. For the special orientation of the Z axis perpendicular to H_0, the twofold rotation symmetry about Z results in a superposition of the resonance from nuclei on sites $B2$ and $A4$, and a similar superposition from those on $B3$ and $A1$.[1] The observed Na^{23} spectrum for $Z\perp H_0$ in the upper nonpolar phase is shown in the top portion of Fig. 2.

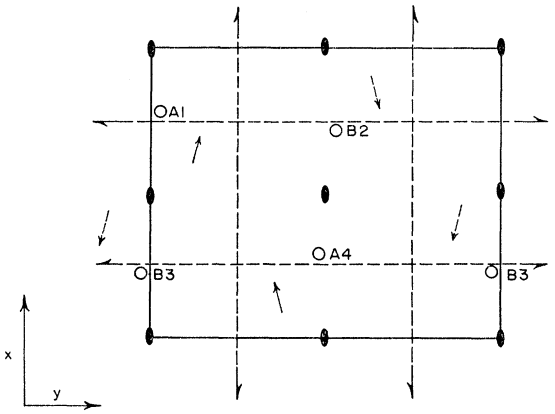

FIG. 1. Projection on the (001) plane of a simplified unit cell of Rochelle salt. The open circles represent the Na^{23} sites. The small arrows indicate the major ferroelectric dipoles. The symmetry operations for the upper nonferroelectric phase (orthorhombic $P2_12_12$) are shown. In the ferroelectric the crystal is monoclinic[9] with symmetry $P2_1$ along x. Sites A and B have slightly different quadrupole coupling constants and asymmetry parameters (see Refs. 1 and 2).

In the polar phase (-18°C$<T<+24$°C) the structure of Rochelle salt is monoclinic $P2_1$ [10], implying that only the twofold screw axis about the X direction remains. For the case of $Z\perp\mathbf{H}_0$ the disappearance of the twofold rotation axis about Z in the polar phase results in each satellite splitting into a pair of satellites.

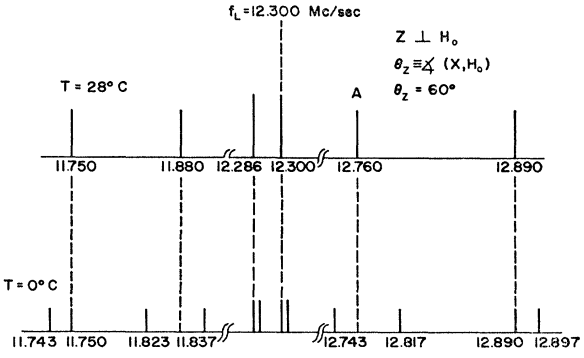

FIG. 2. Complete Na^{23} NMR line spectrum at $+28$°C (top) and at 0°C (bottom) taken with $Z\perp\mathbf{H}_0$ and $\theta_Z=60$°C [$\theta_Z\equiv\angle(X,\mathbf{H}_0)$]. All frequencies are in Mc/sec. The satellite labeled A is followed as a function of temperature (see text).

[26] E. C. Moulton and W. E. Moulton, J. Chem. Phys. **35**, 208 (1961).

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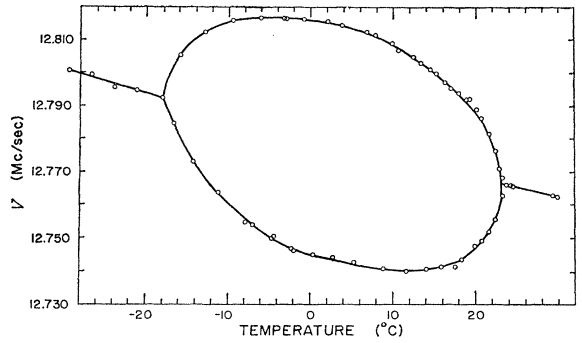

FIG. 3. Location in frequency as a function of temperature of the satellite labeled A in Fig. 2. Satellite A splits into a pair of satellites in the ferroelectric region ($-18°C<T<+24°C$).

The resulting Na^{23} spectrum (at 0°C) is shown in the bottom portion of Fig. 2.

The satellite spectrum itself was used to accurately align the crystal Z axis perpendicular to $\mathbf{H}_0$. All alignments were performed above +24°C. A gross misalignment (>1°) of the Z axis from perpendicularity with H_0 resulted in a satellite being split into a pair of satellites for reasons explained above. Smaller misalignments resulted in excessive linewidths and distorted line shapes.

The satellite line spectrum at 0°C showed the largest relative splitting at $\theta_Z=60°$ (θ_Z is the angle between the X axis and $\mathbf{H}_0$). Consequently this orientation was used in all studies in Sec. III A, unless otherwise noted.

B. Crystal Preparation and NMR Apparatus

The NMR apparatus consisted of a standard P.K.W. oscillator[28] and the usual signal-processing equipment together with a Magnion Ventron (Harvey-Wells) Model L-96 magnet. Frequency measurements were made with a Hewlett-Packard 524D electronic counter.

All Rochelle salt crystals were cut from a large single crystal purchased from Clevite Inc. Samples were generally cut in the shape of a cylinder 12 mm diam and 18 mm long. Crystals to which electric fields were applied were in the shape of plates 18×12×6 mm. Air-drying silver paste was used for electrodes. Electric fields were applied by means of batteries via very light spring contacts. The crystals, when in place in the rf coil, were completely free of any constraints except for the light spring contacts used when external voltages were applied. These light contacts had no effect on the hysteresis loops obtained by the conventional Sawyer-Tower method. The coil assembly was placed in a Dewar flask which was suspended from an adjustable table above the magnet gap, completely free of the magnet. Critical alignments of the vertical axis of the crystal could be performed easily by adjusting the table. This permitted the magnet to be rotated about the crystal and all angles were measured with the large angular scale and vernier on the magnet. Rotation angles could easily be read to within 0.1°. Most experiments were carried out between 0 and +30°C using iso-octane as a coolant. Experiments generally started at 0°C and the temperature was allowed to rise, by itself, toward ambient (+28°C). At low temperatures the warming rate was about 5°C/h but could be slowed, when necessary, by adding small amounts of dry ice. Close to ambient the temperature increased very slowly.

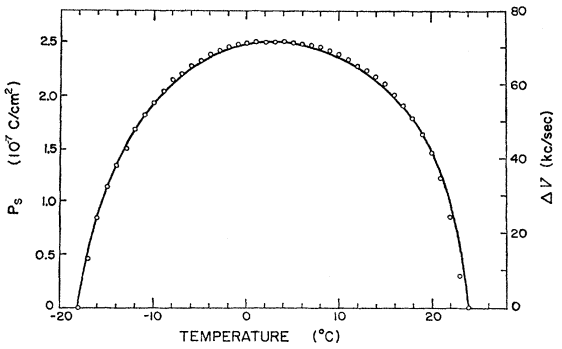

FIG. 4. Satellite line separation in kc/sec as a function of temperature (open circles). The solid line is the polarization as a function of temperature (after Ref. 29) with the corresponding scale on the left. The satellite line separation was normalized to the polarization curve at +3°C. The errors associated with the NMR results are about the size of the open circles.

Typically, experiments covering the range from 0 to +26°C took about 16 h. Temperatures were measured with a chrommel-constantan thermocouple placed next to the sample.

All γ irradiations were performed at 0°C with a Co^{60} source of 10^5 R/h strength located at this school. Samples were transferred from the source to the spectrometer at 0°C. Irradiation times varied from 6 min to 20 h.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. NMR Investigations of Polarization

1. *Temperature Dependence of Satellite Line Separation*

Figure 3 shows the location (in frequency) of a particular satellite line (satellite A of Fig. 2) as a function of temperature with H_0 perpendicular to Z. Above +24°C this satellite is a single line. At +24°C it splits into a pair of satellites of equal amplitude, indicating the onset of the polar phase, and their separation increases rapidly with decreasing temperature, reaching a broad maximum at about +3°C. The satellites begin to converge again as the temperature is lowered further. At −18°C the two satellites superpose again, indicating that the crystal is now in the lower nonpolar phase. In Fig. 4 the satellite line separation (in kc/sec) has been plotted (open circles) as a function

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of temperature. The solid line is a plot of Hablutzel's polarization measurements[29,30] obtained by the conventional Sawyer-Tower bridge method. The NMR satellite-line-separation data has been normalized at the peak separation (~3°C) to the polarization data and the two curves are seen to superpose throughout the polar region. This leads to the conclusion that this satellite splitting is proportional to the spontaneous polarization of the crystal. This result is consistent with the model already used to analyze the Na^{23} quadrupole coupling data in terms of atomic displacements.[1,2]

According to that model, the spontaneous polarization is caused by small displacements of hydroxyl ions and water molecules. The polarization is expected to be proportional to these displacements to first order. These same displacements cause the symmetry of the crystal to be lowered from orthorhombic to monoclinic, and thus split the Na^{23} NMR satellite resonance in two. Then the frequency difference between the members of the resulting doublet is also expected to be proportional,

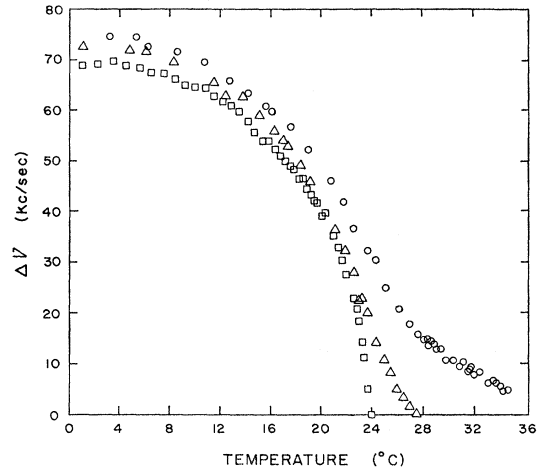

FIG. 5. Effect of an externally applied electric field on the polarization (measured in kc/sec): □=0 V/cm, △=600 V/cm, ○=1380 V/cm.

to first order, to the displacements that cause the polarization. Thus polarization and doublet separation are proportional to each other. The data shown in Fig. 4 and the results given in Sec. III B demonstrate that this is the case.

This method of measuring spontaneous polarization is a truly static method and does not depend on the ability to reverse polarization. Since it has been shown by optical methods[31] that some domains can never be reversed, even at very high applied fields, the NMR method is capable of measuring relative polarizations more accurately than the Sawyer-Tower bridge method.

The NMR data also confirm to a high degree that the phase transition in Rochelle salt is of second order. Discontinuous jumps[32] or coexistence of lines from both phases,[33] which would imply a first-order transition, were not observed close to the transition temperature.

Finally, the NMR method has the advantage that no external connections need to be made to the crystal which might lead to additional, spurious, strain-induced polarization.

2. *Effect of External Electric Fields on Polarization*

From the Devonshire theory[34] of second-order ferroelectric phase transition the effect of an external electric biasing field is to remove the discontinuity in dP_s/dT at the phase transition. It has also been pointed out by Fatuzzo[35] that the presence of a biasing field does not shift or blur a second-order transition; rather, the reversible spontaneous polarization goes smoothly over into the induced (irreversible) polarization above the phase transition.

The results of two such experiments, at applied fields of 600 and 1380 V/cm, clearly demonstrate the smoothing out of the spontaneous polarization at the phase transition and are shown in Fig. 5. The data for the same applied fields but of opposite polarity are not shown for the sake of clarity since it was found that these two curves did not quite superpose with their respective counterparts. This is believed to be due to an "internal bias" present in the crystal and would lead to a shift along the E axis of a hysteresis loop obtained by the Sawyer-Tower method.

Since the electric field is applied at the beginning of the experiment and not removed or reversed during its course, no spurious internal temperature increase of

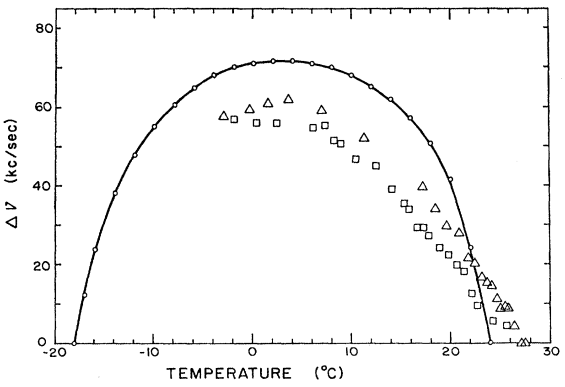

FIG. 6. Effect of a 1.0-MR-γ-ray dose on the satellite line separation (polarization). The uppermost curve is indentical to Fig. 4. The triangles show the satellite line splitting immediately after irradiation. The squares are the data taken after the crystal had been kept at +28°C for two weeks.

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[30] A more recent polarization measurement was done by H. H. Wieder, Phys. Rev. **110**, 29 (1958).
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[34] A. F. Devonshire, Phil. Mag. Suppl. **3**, 85 (1954).
[35] E. Fatuzzo, J. Appl. Phys. **31**, 1029 (1960).

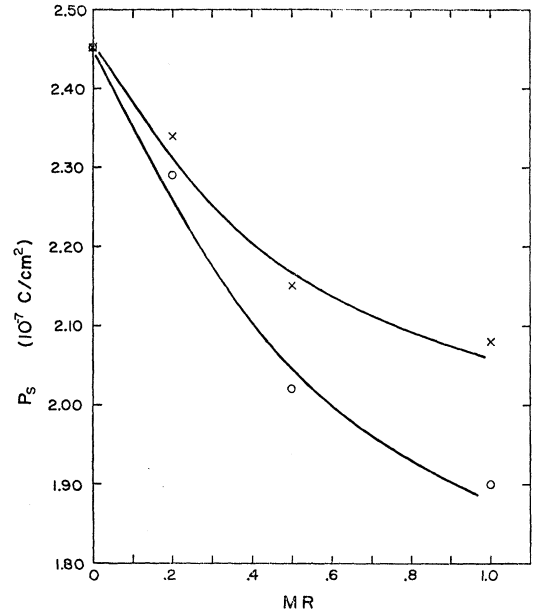

FIG. 7. Polarization (measured by NMR) at +3°C as a function of γ-ray dose. The upper curve shows the polarization immediately after irradiation. The lower curve was obtained two weeks later.

decreases due to the electrocaloric effect[36] are expected. Using this method a very careful investigation of the critical isotherm is being carried out.[37]

3. *Effect of Radiation Damage on the Polarization*

The NMR method of measuring polarization discussed in Sec. III A 1 was used to investigate the effects of ionizing radiation on the polar phase of Rochelle salt. In every case the polarization of the virgin crystal was measured before irradiation. Crystals were then damaged with Co^{60} γ rays at 0°C. Five different dosages of 0.01, 0.2, 0.5, 1.0 and 2.0×10^6 R were used. The first set of data, from 0 to +30°C, was taken immediately after cessation of irradiation. Two weeks later another set of data from 0 to 30°C was taken, the damaged crystal being kept at about 28°C in the interim. Irradiated crystals were slightly yellow, and no attempts were made to keep them shielded from normal room light. No bleaching was observed.

Figure 6 shows the effects of a 1.0-MR dose on the polarization. The uppermost curve is the polarization of the virgin crystal, and the middle curve is the polarization measured immediately after irradiation. It is considerably decreased from the original, indicating that radiation damage has a pronounced effect at the unit cell level. Furthermore, the polarization curve is no longer rounded but almost linear at higher temperatures and extends slightly above +24°C. For the lower doses the decrease in polarization was smaller and no measurable extension above +24°C was observed.

[36] H. H. Wieder, J. Appl. Phys. **30**, 1010 (1959).
[37] E. Fitzgerald and P. A. Casabella (to be published).

The bottom curve is the polarization measured after two weeks of storage at +28°C and shows a further measurable decrease. This effect will be referred to as the after effect and will be discussed in more detail in Sec. III A 4. In Fig. 7 the polarization measured immediately after irradiation (upper curve) and after two weeks (lower curve) are plotted as a function of dosage. For the 0.01-MR dose no measurable differences from the virgin crystal were perceptible. Crystals damaged with a 2.0-MR dose showed only very broad and diffuse satellite lines and no meaningful measurements of satellite separation could be made. Measurements using the Sawyer-Tower bridge method were also performed on these crystals and the results of previous workers were confirmed. In particular, for applied alternating fields up to 1300 V/cm the hysteresis loops for the crystal damaged to 1 MR had disappeared. For lower doses the hysteresis loops were split.

The NMR data confirm the results of Boutin, Frazer, and Jona.[27] In their study of deuterated Rochelle salt, the amplitude of a certain neutron reflection, characteristic of the polar phase, was found to decrease with increasing γ-ray damage. Furthermore, domain structure was observed *above* the phase-transition temperature (35°C for deuterated Rochelle salt) for crystals irradiated in the ferroelectric phase. The NMR results presented here support this result since the satellite lines are still split apart (indicating the crystal structure is polar) above +24°C for Rochelle salt damaged by a 1.0-MR dose. Boutin *et al.* interpreted their results to indicate that radiation damage has both a macrostructural and microstructural effect. The macrostructural effects are (i) clamping or locking of domains resulting in the disappearance of hysteresis loops, and (ii) a slight extension of the polar phase due to defect increased clamping effects which tend to stabilize the crystallographic phase existing during irradiation. The microstructural effect is an actual decrease of the spontaneous polarization at the unit cell level.

Recently, it has been shown by Okada *et al.*[23] (see also Okada[18]) that the hysteresis loops in Rochelle salt could be made to reappear by the application of a suitable external dc biasing field in heavily damaged crystals where formerly it was thought that the hysteresis loops had disappeared. The peaks in the dielectric-constant curve which were broadened and smeared out could also be sharpened up by the same magnitude of external bias. From measurements of dielectric constant and polarization with applied bias it was shown that the width of the ferroelectric region in Rochelle salt had been drastically reduced. For the case of 1-MR dose the transition temperature was found to be between +14 and +16°C. These results can be understood with help of the work of Fatuzzo[35] in ferroelectric Colemanite for which the transition to the ferroelectric phase is also of second order. For the case of Colemanite it was shown that in order to obtain the true ferroelectric transition

temperature from dielectric constant measurements (i.e., the temperature at which the *reversible* spontaneous polarization disappears) one must apply an external biasing field of magnitude and direction to exactly cancel the internal bias inherently present in Colemanite. If the internal bias is not cancelled the dielectric-constant peak is broad and shifted to a higher temperature. Conversely, if no internal bias is present the application of a biasing fields leads to broad and shifted dielectric-constant peaks. It was also pointed out that the application of a biasing field does not shift the true phase-transition point (the temperature at which the reversible spontaneous polarization disappears).

In the case of radiation-damaged Rochelle salt similar effects are present. However, for the case of an initially unpolarized crystal irradiated in the ferroelectric phase it has been shown by hysteresis-loop measurements that approximately half the crystal is biased in one direction and the other half is biased in the opposite direction. If one now desires to find the phase-transition temperature by dielectric-constant measurements one can at best obtain some mean transition temperature because the voltage needed to compensate for the bias in half the crystal is opposite to that required to compensate the other half of the crystal. For half of the crystal one would obtain dielectric peaks which are relatively sharp but for the other half the dielectric peak would be smeared even further and shifted to a still higher temperature. This "composite" dielectric-constant curve would lead to a transition temperature which would probably be too high for the given amount of damage and would also explain why the Curie law is not obeyed for a damaged crystal.

Combining the results of the NMR study with that of Okada *et al.*[23] and of Boutin *et al.*,[27] the main effects of radiation damage in Rochelle salt are now apparent. Radiation damage, besides creating an internal bias, also drastically decreases the width of the ferroelectric phase (the region in which the polarization is reversible), as indicated by the results of Okada. The NMR measurements, which give the total polarization and cannot distinguish between the reversible and irreversible parts, show that the spontaneous polarization is decreased somewhat by the radiation, and for a heavy dose (≥ 1 MR) the polar phase is extended somewhat above the transition temperature of the virgin crystal.

It is because the polar phase still exists well above the temperature at which the reversible polarization disappears for a heavily damaged crystal that the piezoelectric properties of Rochelle salt are now as severely affected by heavy radiation damage as are the ferroelectric properties.[25] This is also the reason why domain structure is still visible even above the transition temperature of the virgin crystal. Pyroelectric measurements should also be able to verify this point. It should also be remarked that in the light of the NMR results and the above discussion, the spontaneous strain induced by radiation damage is considerably more severe than anticipated by Boutin *et al.*[27]

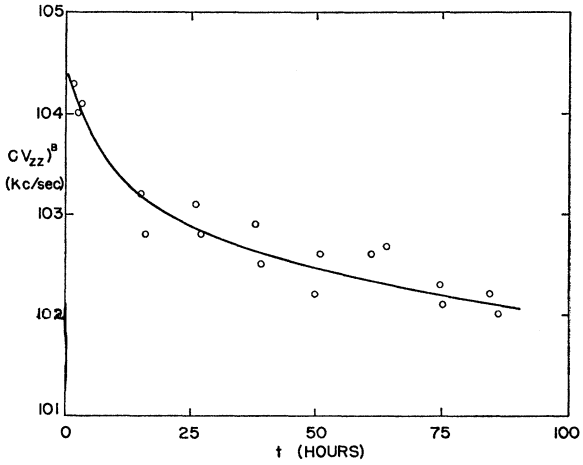

FIG. 8. The magnitude of the zz field-gradient component at the B sites of Na^{23} (see Fig. 1 and Ref. 1) as a function of time after a dose of 1.0 MR of γ rays. All data were taken at $+3°C$ the crystal was allowed to come to ambient temperature between the data points.

In conclusion, it can be noted that the NMR results which give the total polarization have been very useful when combined with the results of Okada, which gave the reversible polarization to delineate the various regions of reversible and nonreversible polarization in damaged Rochelle-salt crystals.

Neutron spectroscopic work could probably yield similar results, but would be time consuming and tedious. X-ray crystallographic studies would not be useful since they are incapable of distinguishing between the polar and nonpolar phases principally because x-ray doses required for crystallographic studies are much larger than those given to the crystals in this study and would very quickly obliterate the polar phase completely.

4. *Aftereffect of Radiation Damage*

In Sec. III A 3 it was noted that the polarization in a damaged crystal continued to decrease for about two weeks after the cessation of irradiation. To study this effect more carefully the crystal was rotated to a special symmetry location with respect to the applied field H_0 which gave the magnitude of only one field-gradient component. Figure 8 shows the magnitude of that field-gradient component, at $+3°C$, as a function of time elapsed after a 1.0-MR irradiation. These data can be correlated with the ESR study of Moulton and Moulton[26] on a single crystal of Rochelle salt. They found that there are three distinct impurity centers produced by x rays in Rochelle salt. Two of these centers decayed over a period of two weeks while the third center grew slowly remaining stable after about two weeks. This stable center was identified as a broken

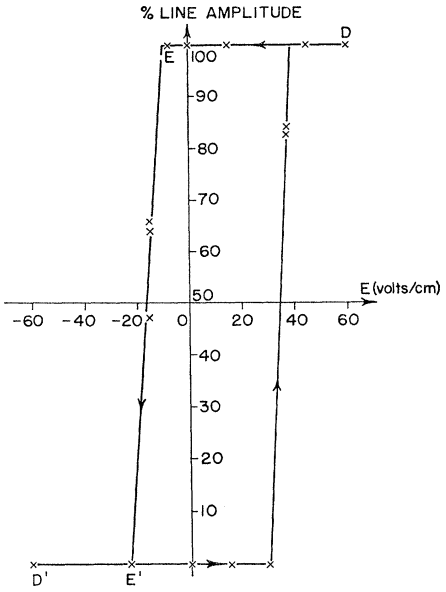

FIG. 9. Quasistatic hysteresis loop obtained by NMR. The relative amplitude (in %) of one satellite of a pair as a function of externally applied electric field. The coercive field is defined as half the loop width. Points D, E, E', and D' are referred to in the text and are concerned with the switching experiments.

C-H bond. The time constant associated with Fig. 8 appears to be of the same order as that involved in the growth of the stable center (broken C-H bond). Therefore, the increasing number of broken C-H bonds appears to be correlated with the decreasing magnitude of the field-gradient component and thus related to the decreasing polarization. The diffusion mechanism which causes continued breaking of C-H bonds long after irradiation has ceased is not understood.

B. NMR Investigation of Domain Structure

1. Effect of Domains on Na^{23} NMR Spectrum

The results up to the present were obtained with the Rochelle-salt crystal accurately aligned with the crystal Z axis perpendicular to the applied field. The results to be described in this section were obtained by deliberately misaligning the crystal Z axis. It was rotated about 8° about the crystal Y axis from the perpendicular position. For the tilted crystal the Na^{23} satellite line spectrum obtained in the higher temperature nonpolar phase (i.e., $T>+24°C$) consisted of four upper and four lower satellite lines because of the inequivalency of the four sodium sites in the unit cell as explained in Sec. II. When the tilted crystal was cooled into the polar (ferroelectric) phase ($-18°C<T<24°C$) the four upper and four lower satellites were expected to shift in frequency but the total number of satellites was expected to remain the same since there are only four Na^{23} atoms per unit cell in all phases. In fact it was observed that in the polar phase each satellite split further into a pair of satellites of roughly equal intensity resulting in a total of eight upper and eight lower satellites. This doubling of the number of satellites can be explained by assuming that one of the pair arises from a site in a unit cell which is in a domain polarized in one direction and the other of the pair arises from the same site but in a domain polarized in the opposite direction. No evidence of domains is present if one of the crystal axes is perpendicular to H_0 since oppositely polarized domains are twins of each other and would go into each other under the two orthorhombic symmetry operations thus leading to identical NMR spectra. To test this an external dc electric field was applied, and for a sufficiently high field one member of each pair had disappeared and the remaining member of the pair was now roughly double in amplitude. Upon reversing the field, the satellite of the pair which had originally disappeared then reappeared and the other of the pair was now gone. This shows that the presence of parallel and antiparallel domains can be observed by the NMR method and is still another indirect method of investigating domains in Rochelle salt.

2. Hysteresis Loops Obtained by NMR

A simple method for tracing out hysteresis loops using Na^{23} NMR satellites was developed based on the results described in Sec. III B 1. The method consists of applying a sequence of increasing voltages to the Rochelle-salt crystal and, after each change of voltage, tracing out the satellite line spectrum for a pair of lines which originate from nuclei in oppositely polarized domains. One of the two satellites begins to disappear and is completely gone at +40 V/cm. The amplitude of one of the two lines is plotted as a function of applied field using the other line amplitude as a reference, since

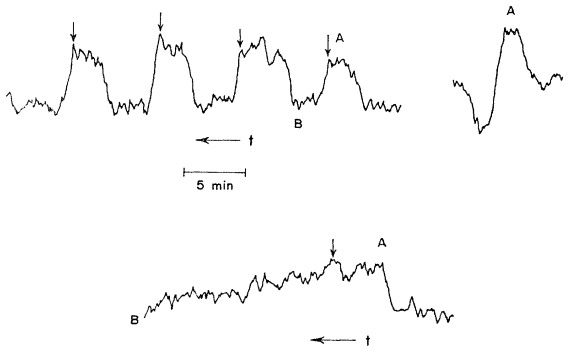

FIG. 10. Results of the dynamic domain-switching experiment. Note that time increases from right to left. Top right shows a typical satellite line from which the switching was carried out. Top left shows repeated switching ($\Delta E_2=52$ V/cm) from the peak of the derivative curve (A). Switching occurs at points indicated by vertical arrows and after each switch the crystal is returned to the original starting place (point E in Fig. 2) via the bottom portion of the hysteresis loop. At point B the spectrometer has returned to the base line. Bottom portion of this figure shows the identical experiment but this time the field has been switched by the amount $E=9.0$ V/cm (the actual switching taking place at the vertical arrow). The return to base line (point B) of the spectrometer in this case was estimated to take about 15 min.

it can be assumed that the sum of the two amplitudes is a constant. An obvious improvement would be to measure integrated intensities of the lines, but the small increase in accuracy did not justify the labor involved. The applied field is then stepped down to -60 V/cm, and the original path from 0 to $+40$ V/cm was not retraced; instead the upper portion of a hysteresis loop was traced out. The field is then stepped back up to $+60$ V/cm, and the hysteresis loop is completed. The result of one such experiment is shown in Fig. 9. Hysteresis loops measured in this fashion take about 10–12 h to complete and are called "quasistatic" hysteresis loops. Hysteresis loops obtained by using the Sawyer-Tower bridge or "normal" hysteresis loops are measured typically at 50 cps or higher.

In the past quasistatic hysteresis loops have been obtained by three other techniques. (i) Ballistic galvanometer methods.[38] This method is tedious and results have poor reproducibility due to charge leakage problems. (ii) Photographing the domain pattern with a polarizing microscope.[39] Results lack accuracy since domains are observed in one focal plane only and might not be representative of the bulk crystal. (iii) The pyroelectric technique of Chynoweth.[40]

The NMR method is advantageous since it is a bulk measurement and the results are very reproducible. The quasistatic loops obtained by NMR are very rectangular, almost resembling ideal loops, and have a very low coercive field: 25 V/cm at $+3$°C for a crystal 0.6 cm thick. At the same temperature the normal loops have a coercive field of about 150 V/cm.[29] The NMR results can be compared with that of Nakamura,[39] who obtained a coercive field of 62.5 V/cm for a crystal 0.06 cm thick and at $+10$°C with optical techniques. Allowing for the dependence of coercive field on temperature, there is an appreciable dependence of coercive field on thickness, showing once more that the coercive field is not a well-defined quantity in Rochelle salt.

3. *Transient Polarization Switching Experiment Using NMR*

In the study of domain dynamics it is of interest to determine how quickly and with what applied field a fully polarized crystal can be reversed into the state of opposite polarization. This was accomplished by using Na^{23} satellite lines in the following manner. The crystal was initially polarized by means of an external field so that only one of the pair of satellites originating from sites in oppositely polarized domains remained. This satellite is shown in the upper right corner of Fig. 10, the crystal being at point D in Fig. 9. The voltage was then lowered to arrive at point E. The spectrometer was run up to the peak of the derivative curve (point A)

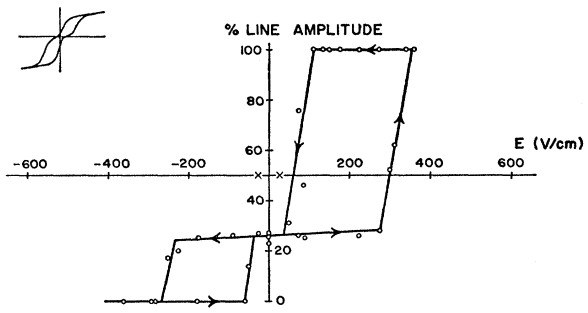

FIG. 11. Quasistatic hysteresis loop in Rochelle salt damaged by 1×10^6R dose of γ rays. ×'s on the abscissa indicate the width of the virgin loop (Fig. 9). Insert in left-hand corner shows a loop obtained by Sawyer-Tower bridge method for the same amount of damage (after Ref. 16).

and the frequency drive was shut off. After a few minutes the crystal was switched from point E to either E' ($\Delta E=9.0$ V/cm) or to D' ($\Delta E=52$ V/cm). When the crystal is switched from E to D' the satellite being studied disappears quickly at the expense of the other satellite (not shown) which is rapidly building up in intensity. The time required for the spectrometer to return to the baseline (point B) was about 5 sec, and was entirely due to the apparatus. The top left portion of Fig. 10 shows a sequence of four such switchings (the crystal being, of course, returned to E from point D' along the bottom portion of the hysteresis loop). This sequence attests to the long-term stability of the spectrometer and the magnet, which were free running. Therefore, for $\Delta E=52$ V/cm the polarization reversal goes to completion in a time considerably less than 5 sec. The bottom portion of Fig. 10 shows the decay of the same satellite but for a switch from E toE' ($\Delta E=9.0$ V/cm). (The actual switching took place at the arrow.) In this case the polarization reversal took about 15 min or 30 times the time constant of the spectrometer.

The NMR results are in qualitative agreement with optical studies[39] which describe the process of polarization reversal as nucleation and slow sideways motion of b and c domain walls. The above results are vastly different from those of pulsing experiments[30] which are described in terms of nucleation and wall propagation in the direction of the ferroelectric a axis. It would seem that reversing the polarization by means of a sine wave field, as in the case when obtaining hysteresis loops by the Sawyer-Tower method, lies somewhere between the two extremes of quasistatic switching and pulsed switching, and should be described by a suitable mixture of both processes.

4. *Quasistatic Hysteresis Loops in Damaged Rochelle Salt*

Quasistatic hysteresis loops in Rochelle-salt crystals, damaged by three different dosages of 0.5, 1.0, and 2.0×10^5 R, were obtained by the NMR method discussed in Sec. III B 2. All data were obtained at $+3$°C. A typical damaged hysteresis loop is shown in Fig. 11

[38] H. Takahasi and J. Hara, J. Phys. Soc. Japan 4, 257 (1949); 4, 261 (1949).
[39] T. Nakamura, J. Phys. Soc. Japan 12, 477 (1957).
[40] A. E. Chynoweth, J. Appl. Phys. 27, 78 (1956).

for a 1.0×10^5 R dose together with a loop obtained by the Sawyer-Tower bridge method for the same amount of damage. The quasistatic loop has a considerable linear portion at the center, whereas the normal loop shows only a small "waist" for the same dosage. This indicates that the slow sideways motion of b- and c-domain walls is considerably more hindered by the defects caused by radiation damage than is the high-mobility reversal processes of wall propagation in the direction of the ferroelectric axis.

IV. CONCLUSIONS

The Na^{23} NMR satellite line separation as a function of temperature in the ferroelectric phase of undamaged Rochelle salt has been shown to be proportional to the polarization as measured by the Sawyer-Tower bridge method, thus calibrating the satellite line separation in terms of the polarization.

The effect of an externally applied electric field is to remove the discontinuity in dP_s/dT at the phase transition as predicted by the Devonshire phenomenological theory. The polar structure induced above 24°C by the electric field is, however, not ferroelectric.

The results of NMR studies in γ-ray-damaged Rochelle-salt crystals show that the spontaneous polarization was diminished by about 20% at 3°C for a 1.0-MR dose. It is estimated that roughly 3% of the unit cells are damaged by this dose. In addition this amount of damage extended the polar phase slightly above the transition temperature of the virgin crystal.

The results of polarization measurements by the Sawyer-Tower bridge method (which measures only the amount of *reversible* polarization) indicates, on the other hand, that the ferroelectric phase has disappeared at around +14 to +16°C for this amount of damage. Combining these results it is therefore clear that for a given amount of damage the ferroelectric region (the region of reversible polarization) decreases but that there is still a considerable region in the P-versus-T plane (even above T_c for heavy doses) when the polar structure is still present although the polarization is no longer reversible. Therefore, radiation damage, besides decreasing the ferroelectric region, also introduces a very large strain tending to stabilize the polar phase. This also explains why the piezoelectric properties of Rochelle salt are not as severely affected by the damage as are the ferroelectric properties and why the domain structure is still present even above T_c for heavy damage.

The NMR data also showed that the polarization continues to decrease for a considerable time after the cessation of irradiation and that this continued decrease can be correlated to a continued breaking of C-H bonds in the structure.

For a slightly different orientation of the Rochelle-salt crystal with respect to the external magnetic field, a completely different set of experiments was possible. Thus closely spaced satellite doublets were shown to arise from oppositely polarized domains and quasistatic hysteresis loops using NMR were obtained.

The hysteresis loops obtained in this manner are similar to those obtained by optical methods and indicate that polarization reversal as measured by NMR goes to completion via the slow sideways expansion of b- and c-domain walls. There also exists a "critical" or "threshold" field, which depends to some extent on temperature and sample thickness, below which no polarization reversal can take place. Once the "critical" field is exceeded the reversal goes to completion in a time which depends upon the difference between applied and critical fields. Furthermore, quasistatic hysteresis loops are very rectangular and have a very low coercive field compared to normal loops obtained by the conventional Sawyer-Tower bridge method. Radiation damage also affects the quasistatic loops much more seriously than the normal loops, indicating that the slow sideways motion of b- and c-domain walls is considerably more hindered by the defects introduced by radiation damage than is the reversal process by way of nucleation and propagation of wedge-shaped domains in the ferroelectric direction.