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NMR Studies of Domain Switching in Ferroelectric Rochelle Salt[*]

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ABSTRACT

The Na^{23} NMR satellite line spectrum in the ferroelectric phase of Rochelle Salt is used to obtain hysteresis loops and to investigate the relation between the rate of polarization reversal and the change of externally applied electric field.

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Several investigators have observed nuclear magnetic resonance (NMR) quadrupole satellite lines split into closely spaced doublets in the ferroelectric phases of Rochelle Salt (RS)[1], KH_2PO_4[2] and KD_2PO_4 [3]. The relative intensity of the two components of the doublet could be altered by applying an external dc electric field along the ferroelectric axis[1,2]. These experiments verified that the two components of the doublet arose from nuclei at identical crystallographic sites but in oppositely polarized domains.

In this letter the first domain switching experiment in a ferroelectric crystal using NMR satellite lines in reported[4]. It is shown that the Na^{23} ($I = 3/2$) NMR satellite line spectrum in the ferroelectric phase of RS can be utilized to obtain hysteresis loops. Hysteresis loops observed in this manner are drastically different from the conventional hysteresis loops ("normal loops") obtained by the usual Sawyer-Tower bridge method[5]. It is further demonstrated that the NMR method can also be used to perform dynamic switching experiments to investigate the dependence of the rate of polarization reversal on the change of applied electric field.

Rochelle Salt is ferroelectric only between $-18°C<T<+24°C$ and is structurally very complex[6]. The detailed structural analysis has not been completed. Na^{23} NMR investigations[1,7] have successfully verified the proposed[8] ionic dipole displacements responsible for ferroelectricity in RS. Figure 1 shows two simplified unit cells of RS polarized in opposite directions together with the symmetry operations for the non-ferroelectric, orthorhombic phase ($T>+24°C$). The open circles represent the four Na^{23} sites and the arrows are the major ferroelectric dipoles.

The ferroelectric domain structure of RS is, nevertheless, relatively simple. Domains are slabs parallel to ab plane (b-domains) or slabs parallel to ac plane (c-domains) of parallel or anti-parallel polarization along the a-axis[9]. No significant differences have been detected in the dynamics of b- and c-domains.

The Na^{23} NMR spectum in the higher temperature non-ferroelectric phase has eight quadrupole satellite lines; one pair for each of the four physically inequivalent Na^{23} sites per unit cell. Upon cooling into the ferroelectric phase, each satellite was observed to shift frequency and split into a closely spaced doublet, with the doublet spacing dependent on the orientation of the crystal. An external dc electric field in the direction of the ferroelectric a-axis removed one member of each doublet, the remaining member growing to twice its original intensity. Upon reversing the electric field the lines which had originally disappeared, reappeared, and the other member of each doublet had now disappeared verifying that the splitting was indeed caused by ferroelectric domains. No evidence of domains is present if one of the crystal axes is perpendicular to H_o 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.

The results presented here were obtained on crystal plates (thickness = .6 cm) whose z axes were tilted about 8° from perpendicularity with H_o. The experiments were performed at +3°C using a conventional P.K.W. spectrometer with applied voltages supplied by batteries. A typical hysteresis loop, shown in Fig. 2, was obtained by scanning the spectrometer frequency over both members of a suitable doublet and plotting the peak-to-peak amplitude of one member of the doublet using the other member as amplitude reference since it can be assumed that the sum of the two amplitudes is a constant.

The applied voltage was maintained across the crystal throughout the experiment and the spectrometer was scanned through the doublet each time the voltage was changed. The tracing out of the complete loop took up to 12 hours and will be called a "quasi-static" loop. The slight shift along the E-axis is probably due to a small amount of internal bias.[5]

Quasi-static loops obtained by NMR are very rectangular with a very low coercive field of about 25 V/cm. The "normal" loops obtained at +3°C with sine wave field of 50 c/sec or higher have coercive fields of about 150 V/cm[10,11] are are considerably more rounded.

The dynamic domain switching experiments were performed by first polarizing the crystal to the point D in Fig. 2, lowering the field to arrive at point E and then switching from E to E' ($\Delta E_1 = 9.0$ V/cm) or to D' ($\Delta E_2 = 52$ V/cm). At point E only one satellite of the pair is present and the spectrometer was driven up to the derivative peak of this line (point A Fig. 3) and the frequency drive was shut off. After a few minutes the electric field was switched (at the point indicated by the vertical arrow) by the amount ΔE_2, and the satellite on which the spectrometer was sitting decayed rapidly at the expense of the other satellite (not shown) which was building up in amplitude. The spectrometer reached the base-line (point B Fig. 3) in about 5 sec. This decay time is entirely due to the time constant associated with the spectrometer. Four cycles of switching from point E to D' (the crystal being returned to point E along the bottom portion of the loop) are shown at top left of Fig. 3. This trace attests to the long term stability of the spectrometer and magnet which were completely free-running. The bottom portion of Fig. 3 shows a typical trace of a switch from E to E' ($\Delta E_1 = 9.0$ V) (the actual switching took place at the point indicated by the vertical arrow). The polarization reversal in this case took about 15 minutes to complete.

Previous polarization reversal experiments in RS were performed by two very different techniques yielding also two very different results. The optical experiments of Nakamura,[12] using a polarizing light microscope, showed that the polarization reversal in RS took place via slow sideways expansion of b- and c-domain walls, that there exists a "critical" or "threshold" field, E_o, below which no reversal can take place, and that once E_o was exceeded the switching time τ was given by $1/\tau \; \alpha (E-E_o)$. From these results a domain wall mobility, $\mu = 1.36 \times 10^{-3}$ cm^2 V^{-1} sec^{-1}, was determined.

The NMR results presented here are in very good qualitative agreement with Nakamura's results. Furthermore, the NMR results are very reproducible and are a bulk measurement. The lack of quantitative agreement, especially with regard to differences in E_o between the two experiments is not serious and can be attributed to differences in crystal thicknesses and to differences in the temperatures between the two experiments. Also the optical experiments give results in one focal plane only which might not be representative of the bulk crystal.

Vastly different results were obtained by Wieder[11] who investigated polarization reversal by applying very fast rise-time pulses of alternating polarity to the crystal. No "critical" field was observed down to fields of 10 V/cm and domain wall mobilities were calculated to be 110 cm^2 V^{-1} sec^{-1}. In the case of fast pulsing experiments the polarization reversal is believed to be by nucleation and wall propagation in the ferroelectric axis direction which is evidently a much faster process than the sideways expansion of b- and c-domain walls. It would seem therefore, that reversing the polarization by means of a sine wave field, as in the case when obtaining hysteresis loops by the Sawyer-Tower bridge method lies somewhere between the two extremes of "quasi-static" switching and pulsed switching and should be described by a suitable mixture of both processes. Hence the rate of change of applied field (virtually zero for quasi-static switching and extremely high for pulsed switching) seems to determine which process predominates.

In conclusion, it is seen that the NMR results on polarization reversal in RS parallel the results of the optical work of Nakamura and that the NMR method gives results on polarization reversal via the slow sideways motion of b- and c-domain walls. Furthermore, the NMR methods discussed in this letter should also prove useful in the investigations of quasi-static polarization reversal in many other ferroelectrics such as guanidine aluminum sulfate hexahydrate (GASH) and related compounds, deuterated triglycine sulfate (DTGS), and isomorphs, etc. in which domain structures cannot be observed by the polarizing light microscope method without straining the crystals[5], or in KH_2SO_4, KD_2SO_4 and isomorphs in which the ferroelectric phase appears only at relatively low temperatures thus presenting formidable experimental problems for microscope work.

FOOTNOTES

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FIGURE CAPTIONS

Fig. 1. Projection on the (001) plane of two simplified unit cells of Rochelle Salt polarized in opposite directions. The open circles are the Na^{23} sites. The small arrows are the major ferroelectric dipoles. The symmetry operations for the upper non-ferroelectric phase (orthorhombic $P2_12_12$) are shown. In the ferroelectric phase the crystal is monoclinic with symmetry $P2_1$ along a. Sites A and B have slightly different quadrupole coupling constants and asymmetry parameters (see Ref. 1 and 7).

Fig. 2. A hysteresis loop obtained by NMR. The relative amplitude (in %) of one satellite of the doublet 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 dynamic switching experiment.

Fig. 3. Results of the dynamic domain switching experiment. Note that time increases from right to left in this figure. 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 $\Delta E_1 = 9.0$ V/cm (the actual switching taking place at the vertical arrow). The return to base line (point B) of the spectrometer in this case took about 15 minutes.

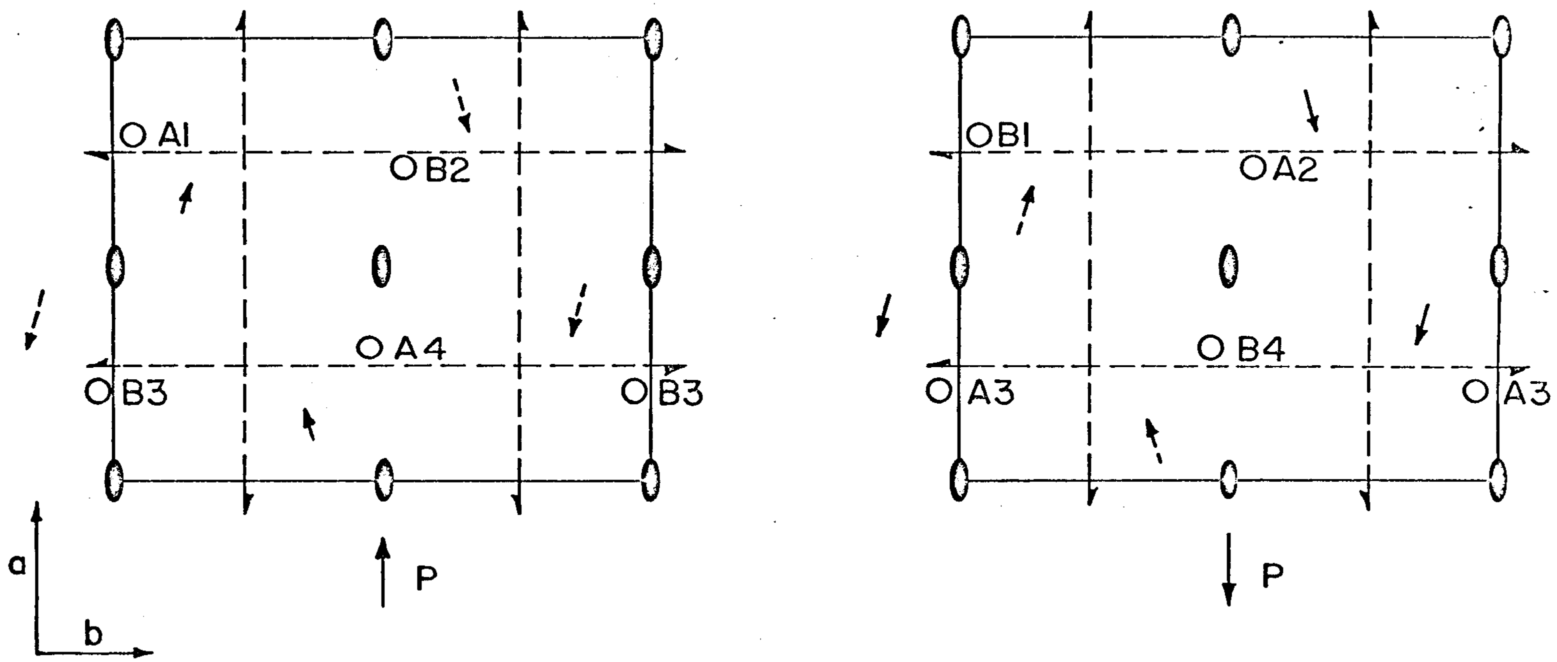
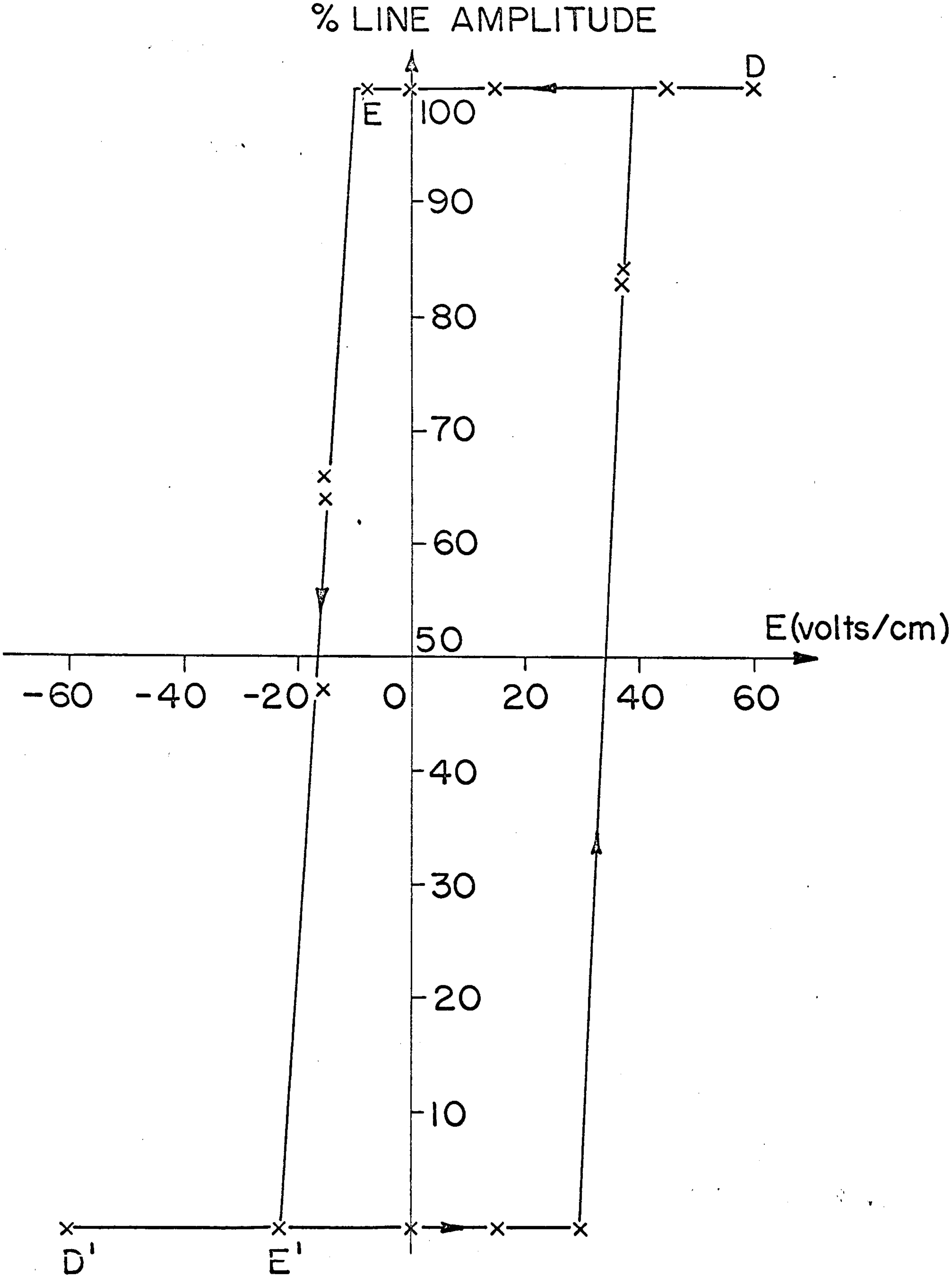


Fig. 1



% LINE AMPLITUDE
D
E
100
90
80
70
60
50
E(volts/cm)
-60
-40
-20
0
20
40
60
40
30
20
10
D'
E'

Fig. 2

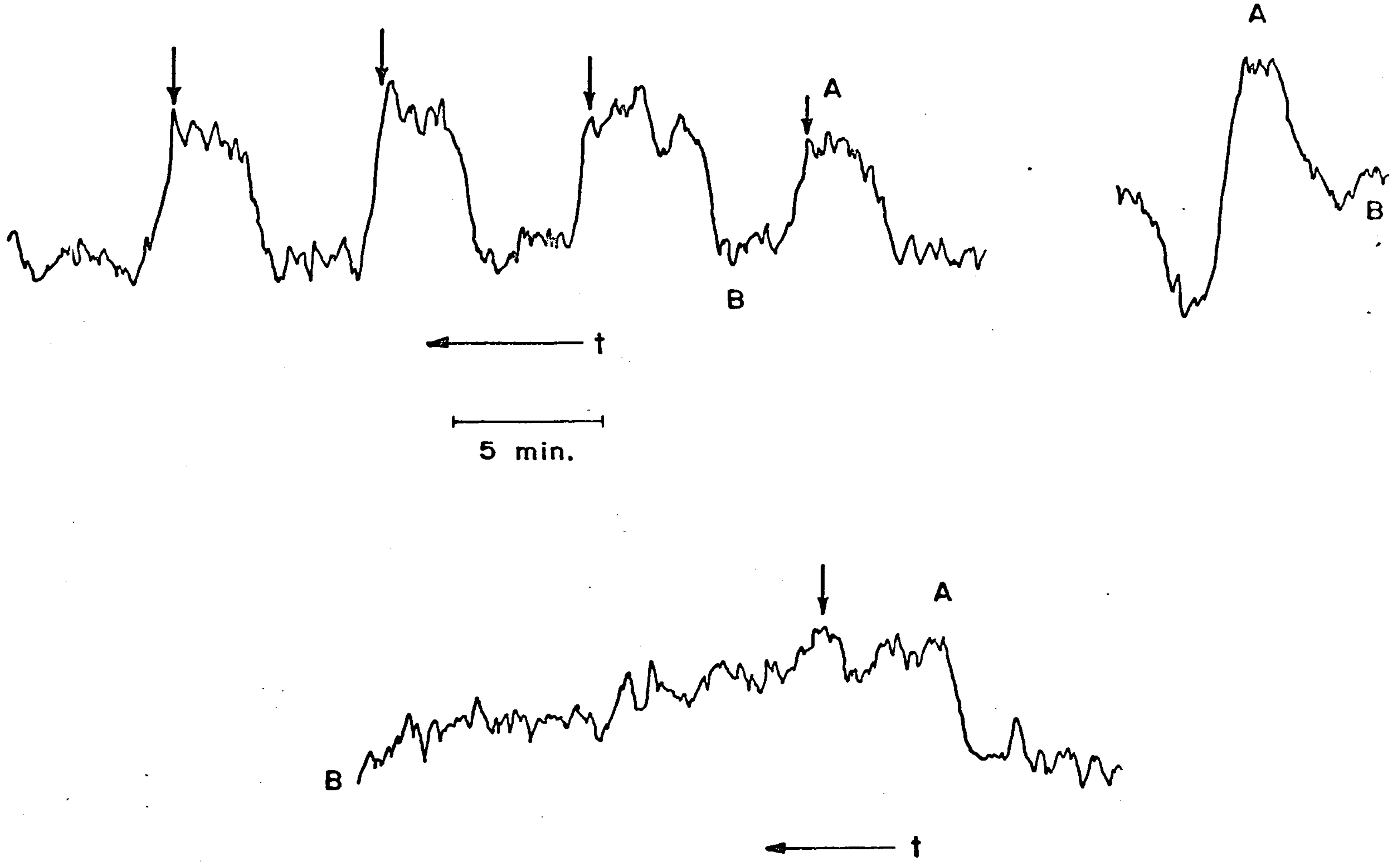


Fig. 3