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# Rochelle salt in an inhomogeneous electric field

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**Abstract.** The parameters of the hysteresis loop in the ferroelectric Rochelle salt were investigated using a sample with two pairs of electrodes: measurement electrodes and the side ones. It has been shown that the difference between the potentials of the measurement and the side electrodes (generating an inhomogeneous electric field) leads to gradual decay in time t of the remanent polarization $P_r$. The time required for the hysteresis loop to disappear in the inhomogeneous electric field (not parallel to the ferroelectric axis) decreases with temperature increase from $44 \pm 3$ h at –9 °C to $2.3 \pm 0.1$ h at 21.9 °C. On the other hand, the crystal placed for a sufficiently long time simultaneously in the measuring electric field and in the constant inhomogeneous one may finally exhibit a stationary hysteresis loop with a reduced remanent polarization and the unchanged coercive field. It has been shown that the crystal as a whole does not have to be polarized perpendicularly to the ferroelectric axis in order for its hysteresis loop to be reduced.

**PACS.** 77.80.-e Ferroelectricity and antiferroelectricity – 77.80.Dj Domain structure; hysteresis – 77.80.Fm Switching phenomena

## 1 Introduction

Due to the possibility of practical application of ferroelectrics the hysteresis loop parameters have been intensively investigated for years. Within this scope fall papers that aim at determining the influence of the measuring field's amplitude and frequency as well as temperature, pressure and a constant electric field on the shape and the position of the loop [1–3]. What is equally important is the research intended to define the influence of admixtures and defects, X- and $\gamma$- radiation as well as pale irradiation [4–7]. What appears particularly interesting is the research into the molecular mechanism of loop deformation and the creation of a bias field. These effects take place in time usually in a gradual manner under the influence of a sufficiently long-lasting factor. One could take here as an example the gradual appearance of the bias field or the loop splitting caused by X-radiation or pale irradiation, which at longer irradiation times resulted even in the loop disappearance. These effects have been shown in the classic papers by Chynoweth [4] and Fatuzzo [6].

As recently found out, also the application of a prolonged electric field perpendicular to the ferroelectric axis leads to a gradual reduction or even disappearance of the hysteresis loop in the triglycine sulphate (TGS) and Rochelle salt crystals ([8–11] and cited therein). If, however, after the disconnection of such a field, the sample is placed in a driving electric field (parallel to the ferroelectric axis, as in the Sawyer-Tower method), the original hysteresis loop can be restored. Although the time of such a gradual rejuvenation is relatively long, the hysteresis loop measured then cannot be considered as a stationary one. The conclusion arises that in order for some kind of dynamical equilibrium conditions to be achieved both driving electric field and the transverse constant one should be simultaneously applied.

The present paper provides the evidence that the values of the remanent polarization $P_r$ of the Rochelle salt can be programmed from the interval $0 \leqslant P_r \leqslant P_{r0}$ at a constant temperature and measured then in stationary (dynamical equilibrium) conditions, where $P_{r0}$ is the remanent polarization of the original sample (fully rejuvenated). It will be additionally shown that the sample as a whole does not have to be transversely polarized (cf. [12]) in order for its hysteresis loop to be reduced.

## 2 Experiment

During the hysteresis loop measurements, apart from the driving field acting due to the potential $V_m$ application, the crystal was simultaneously exposed to an inhomogeneous constant electric field. Such a case could be accomplished when not only the measurement electrodes (perpendicular to the ferroelectric $a$-axis) potential but also the potential of the sample's side walls was controlled. For this purpose, additional stripe-like grounded electrodes (perpendicular to the pseudorhombic $b$-axis [13], [10]) were attached to both side walls of the crystal, as shown in insert of Figure 1. These new electrodes were connected to

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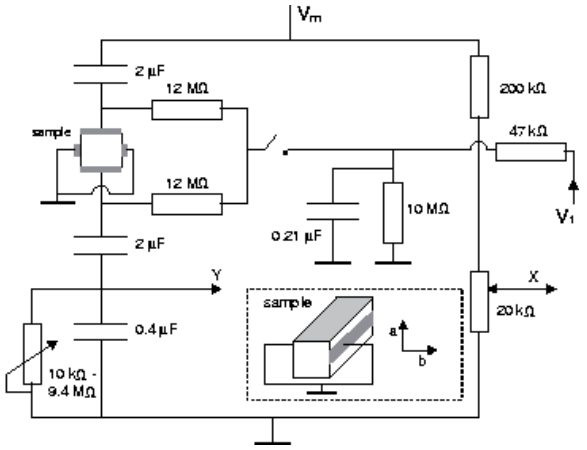


**Fig. 1.** Measurement circuit; insert: sample with electrodes, the arrows indicate the ferroelectric $a$-axis and the pseudorhombic $b$-axis.

each other and their potential was equal to zero. On the other hand, the potential of both measurement electrodes was raised by the same constant value $V_f > 0$. For this purpose the arrangement applied within the Sawyer-Tower method was supplemented by two blocking capacitors of 2 $\mu$F each. It should be pointed out that in the presented case the time mean value of the resultant polarization of the crystal can be assumed to be equal to zero.

The voltage between the measurement electrodes and the side ones has decisive impact on the observed remanent polarization value. One could notice both similarities and differences between the effects of the inhomogeneous electric field action resulting from the difference of potentials of the two pairs of electrodes, and the effects of irradiation, doping and the application of hydrostatic pressure.

The ferroelectric hysteresis loop (polarization $P_{||}$ a versus $E = V_m/d$) of a Rochelle salt single crystal has been measured at different temperatures and for various values of $V_f$. Insert of Figure 1 presents the investigated sample together with the electrodes of the appropriate potentials, shown schematically. The sample dimensions were 13.1 mm × 4.8 mm ×5.2 mm, the distance between the measurement electrodes was $d = 5.2$ mm and the side electrodes width was 1.5 mm. The main part of Figure 1 depicts the measurement circuit.

## 3 Results

Figure 2 shows the process of the hysteresis loop complete decay due to the application of the long-lasting constant potential $V_f = 1000$ V at the temperature of 15 °C (as commonly known, the ferroelectric phase in the Rochelle salt is observed between $T_{C1} = -18$ °C and $T_{C2} = 24$ °C). Along with the potential $V_f$, the sinusoidal driving voltage $V_m$ of the frequency $f = 100$ Hz and the amplitude 250 V was being continuously applied, even between successive loop measurements. The observable changes in the remanent polarization could be described by the function

$$P_r(t) = P_{r0}\frac{t_d - t}{t_d}\exp(-t/\tau_E) \qquad (1)$$

where $t_d$ is the time after which the hysteresis loop disappears. The times $t_d$ and $\tau_E$ depend on temperature. Insert of Figure 2 shows the fitted values of $t_d$ as a function of temperature. The corresponding relaxation times $\tau_E$ are: $44 \pm 9$, $20 \pm 4$, $3.3 \pm 0.7$ and $1.9 \pm 0.6$ h for –9, 3.1, 15 and 21.9 °C, respectively. It should be stressed that no changes in a coercive field values are visible as the remanent polarization decreases.

Although the time after which $P_r$ disappears seems to be influenced by an actual domain structure and it may depend on the sample history, a reduction of $t_d$ and $\tau_E$ at rising temperature from below the polarization maximum to above it (within the ferroelectric phase) is quite an interesting result, considering the crystal with two critical points.

After the reduction of the potential $V_f$ to zero the hysteresis loop may be invisible for a few hours. Afterwards, it reappears and increases gradually, less and less rapidly, but the coercive field still remains unchanged. If the driving field is being applied, such a restoration takes place more rapidly. For example, at 15 °C the remanent polarization returns from zero to its original value after about 200 h, when the driving voltage (with the amplitude of 250 V and frequency of 100 Hz) is continuously applied. The time dependence of $P_r$ is similar to that shown in Figure 3, and the difference consists only in the fact that the saturation for $V_f = 0$ is achieved on the dotted line level denoted by '$V_f = 0$ V'.

If the sample with the reduced remanent polarization is kept in a zero electric field, the restoration to the original state seems to be very slow. What is more, it cannot be said if such a sample will at any time return to its state before the inhomogeneous electric field application unless it is heated above the upper critical point $T_{C2}$. An annealing above the $T_{C2}$ temperature leads to the crystal rejuvenation, independently of whether or not any driving field is applied.

Using the measurement circuit shown in Figure 1 we can control the remanent polarization value by means of the potential $V_f$. As mentioned above, the coercive field remains unchanged then. Figure 3 shows the influence of $V_f$ on the remanent polarization for $T = 21.9$ °C. The driving voltage (with the amplitude of 250 V and frequency of 100 Hz) was applied continuously. Because the process of $P_r$ suppression seemed to be more effective for higher $V_f$ values (cf. [11] for TGS), it was convenient to reach the initial state with the zero remanent polarization by applying the potential $V_m = 1000$ V. Next, the value of $V_f$ was decreased to 100 V. Not even such a reduction of $V_f$ did result in an appearance of any non-zero remanent polarization (within the limits of experimental errors). However, after further reduction of $V_f$ to 50 V the hysteresis loop could be observed. The time dependence of $P_r$ observed after the change from $V_f = 100$ V to $V_f = 50$ V is shown in Figure 3, where $t = 0$ corresponds to the moment when

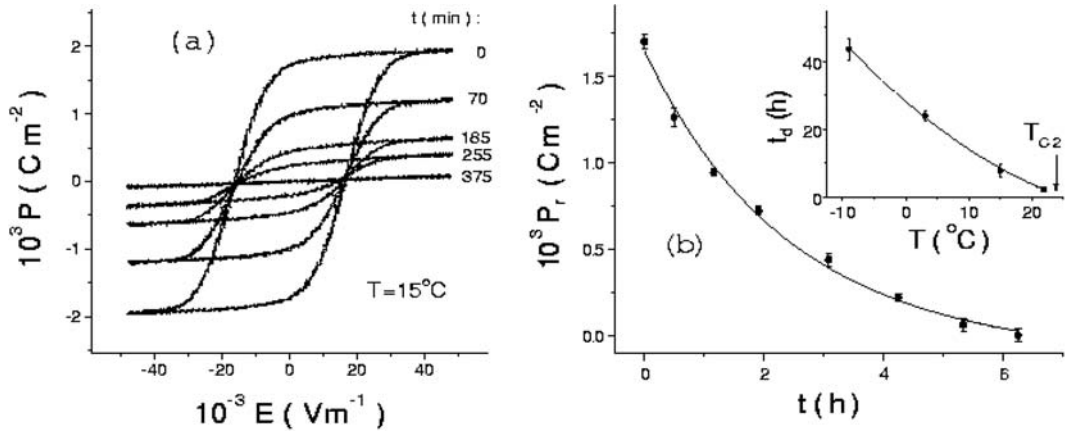


**Fig. 2.** Decay in time of remanent polarization in the prolonged inhomogeneous electric field, i.e. for $V_f = 1000$ V at $T = 15$ °C: hysteresis loops (a) and $P_r$ versus $t$; solid line represents a numerical fit (Eq. (1)) to the experimental points; insert: time $t_d$ as a function of temperature (b).

$V_f$ switches to 50 V. The solid line in the main diagram of Figure 3 denotes the exponential function fitted to the experimental data obtained at $T = 21.9$ °C

$$P_r^{(50)} = P_{rs}^{(50)}\{1 - \exp[-t/\tau^{(50)}]\} \qquad (2)$$

where $\tau^{(50)} = (45 \pm 2)$ h and $P_{rs}^{(50)} = (0.59 \pm 0.01) \times 10^{-3}$ cm$^{-2}$. As follows from the experimental data, different hysteresis loops could be observed in the stationary conditions (after saturation), depending on the $V_f$ value. As mentioned above, after disconnecting $V_f$ the remanent polarization slowly relaxes to its original value. For $0 < V_f < 100$ V the partially reduced loops are observed in saturation. Inset of Figure 3 presents three hysteresis loops measured in saturation for $V_f = 0$, 50 and 100 V.

The problem is that the time of $P_r$ restoration is too long. Diminishing its value, e.g. by a different way of applying the potentials $V_m$ and $V_f$ or by a reduction of the sample dimensions and shape, requires investigations. It is worth adding that the remanent polarization cannot be controlled in such a way by means of temperature only as it would induce a change in the coercive field.

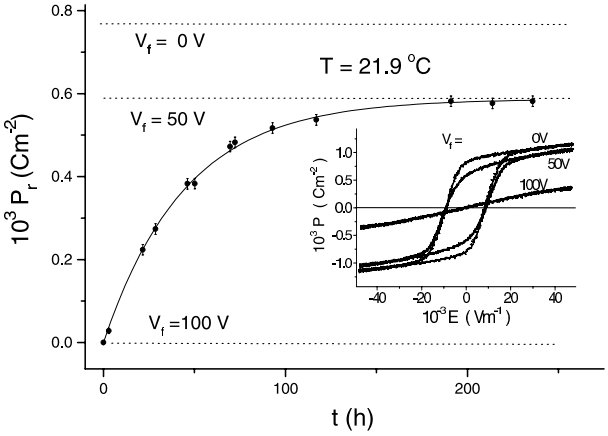


**Fig. 3.** Restoration in time of the formerly fully reduced remanent polarization at $T = 21.9$ °C when applying the potential $V_f = 50$ V; dotted lines represent the saturation levels for $V_f = 0$, 50 and 100 V; insert: the corresponding hysteresis loops in saturation.

## 4 Discussion

There are a lot of indications that under the influence of an inhomogeneous electric field there occurs a gradual "freezing" of ever more groups of dipoles, probably stabilized by a space charge (the role of the space charge has not been explained in detail so far). This means that ever larger parts of the sample are gradually assuming a metastable state. Consequently, fewer and fewer dipoles are being repolarized in the alternating field. The relation (1) is the solution of a differential equation:

$$\frac{d^2y}{dt^2} + \frac{2}{\tau_E}\frac{dy}{dt} + \frac{1}{\tau_E^2}y = 0, \qquad (3)$$

for $y = P_r(t)/P_{r0} > 0$, $P_{r0} = P_r(0)$, $y(0) = 1$ and $dy/dt|_{t=0} = -(\tau_E^{-1} + t_d^{-1})$. This is a critical damping case in the harmonic oscillator theory. In the experiment described above, obviously only positive values of the function $y(t)$ were measured. Due to the validity of formulae (1) and (3) we can distinguish two mechanisms (with two characteristic times $\tau_E$ and $t_d$) which are responsible for the remanent polarization decay in time. Because the coercive field remains unchanged during the prolonged potential $V_f$ application the following interpretation seems to be reasonable. The exponential part in formula (1) describes the decay in time of the polarization due to a nucleation of small frozen regions here and there in the sample. Consequently, the number of still active dipoles which are being repolarized decreases exponentially. However, at the same time the small frozen nuclei grow linearly with time, which also leads to a reduction of switchable polarization. The latter mechanism is described by the linear part of formula (1). For $t_d \gg \tau_E$ the "almost" exponential $P_r$(t) dependence can be observed. On the other hand, the relation

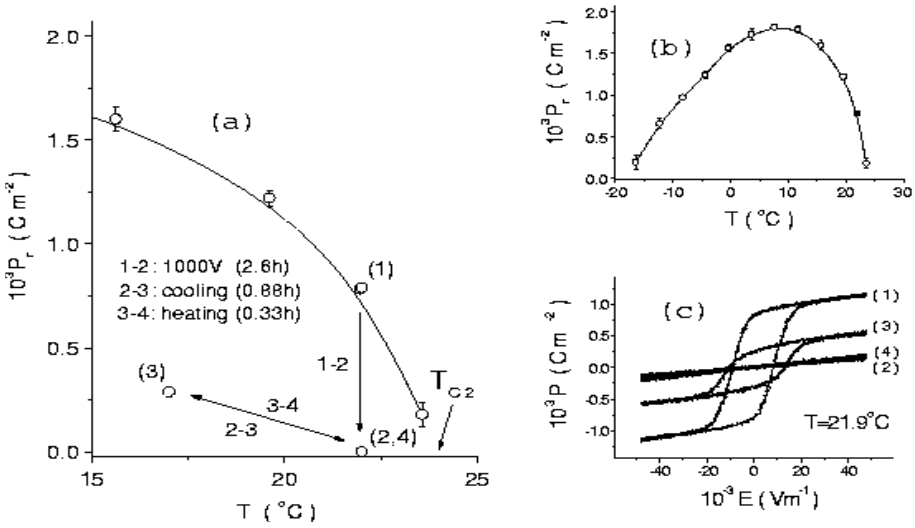


**Fig. 4.** Temperature dependence of $P_r$ of the rejuvenated (original) sample (circles connected by a solid curve); decrease in $P_r$ at the constant temperature $T = 21.9$ °C for $V_f = 1000$ V (1–2), cooling (2–3) and heating (3–4), both for $V_f = 0$ (a); temperature dependence of $P_r$ of the rejuvenated sample (b); hysteresis loops observed at the points (1)–(4) (cf. Fig. 4a) (c); solid lines are made by a cubic B-spline connection.

$\tau_E \ll t_d$ implies that the linear component is dominant. In experiment both mechanisms are usually detected simultaneously. The value of velocity $1/t_d$ is one of the initial conditions formulated for the differential equation (3) and can be different for various samples with different domain structures.

After the disconnection of $V_f$, indeed, there begins a transition to a stable state. However, this is a very lengthy process. The majority of frozen dipoles still remain confined in the metastable state for days. The experimental results shown in Figure 4 justify such an interpretation. If a "frozen" sample, i.e. not exhibiting the hysteresis loop, is cooled by a few degrees, a small loop may actually appear; but if the previous temperature is restored by heating, the loop disappears again. At the temperature $T = 21.9$ °C $< T_{C2}$ the sample was exposed to an inhomogeneous field ($V_f = 1000$ V) for 2.6 h (1–2, see Fig. 4), which caused the complete loop decay. Then the sample was cooled down to $T = 17$ °C at $V_f = 0$ (2–3), which generated some non-zero remanent polarization. Finally, the crystal was heated up to $T = 21.9$ °C (3–4), which resulted in the loop disappearing again. In the course of the experiment (a few hours) the sample was obviously undergoing a slow gradual rejuvenation, mainly due to the continuous action of the measuring field. This fact is connected with a transition, accelerated by the driving field, from the metastable states mentioned above to the stable ones. This process was so slow, however, that it caused only a slight increase (hardly visible in the figure) in the average slope of the polarization $P$ versus the measuring electric field $E$ dependence at the final temperature $T = 21.9$ °C. The above results imply that after switching off the potential $V_f$, cooling and then heating the sample the loop may disappear at a temperature lower than the one of the upper critical point $T_{C2}$. The remanent polarization in the zero electric field is then temperature-dependent and it declines completely in such a way as if the phase transition occurred at a temperature lower than $T_{C2}$. As follows from the investigations carried out so far, a situation is possible in which after a sufficiently prolonged inhomogeneous field action (a few degrees below $T_{C2}$) the hysteresis loop can be observed for $V_f = 0$ for hours only in the considerably narrowed temperature interval between $T_{C1}$ and $T_{C2}$ (cf. [10,14]).

An important experimental fact shown in Figure 2 is that the coercive field remains unchanged as the remanent polarization gradually decreases in time due to the application of a non-zero potential $V_f$. Such behaviour was also observed in triglycine sulphate in a prolonged electric field not parallel to the ferroelectric $b$-axis [12], [11]. There is every indication that the ferroelectrics TGS and the Rochelle salt behave in a very similar manner in an electric field not parallel to the ferroelectric axis. In a work on TGS and TGFB under high pressure [3] a very similar behaviour pattern was ascertained, i.e. a decrease with time in the remanent polarization not accompanied by any changes in the coercive field. Such an effect could be observed for pressures higher than 20 kbar. However, on removal from a high-pressure vessel, the sample fell to pieces as a result of penetration by a pressure-converging medium. The effect shown in Figure 2 of the present paper is reversible.

Apart from the results for TGS and the Rochelle salt in the transverse electric field and the experiment under high pressure mentioned above, no other experimentally observed process of the remanent polarization gradual decay without changes in the coercive field is known to the author of the present paper. The influence of a space electric charge and charged defects on the shape of the hysteresis loop have been intensively investigated theoretically in recent years, both in bulk ferroelectrics and in films. A simultaneous reduction of the remanent polarization and

the coercive field was usually ascertained (e.g. [15,16]). An exception is the work by Bratkovsky and Levanyuk [17] where the coercive field changes in ferroelectric films could be neglected.

## 5 Conclusions

Summing up the results of this paper one can state that:

1. Stationary hysteresis loops with different remanent polarization values $0 < P_r < P_{r0}$ can be programmed by adjusting the potential $V_f$ and the measuring field parameters, at a given temperature within the ferroelectric phase; the coercive field remains unchanged then.
2. The higher the temperature (within the ferroelectric phase), the more effective is the process of the hysteresis loop decay in the sample placed in a prolonged inhomogeneous electric field.
3. The effects generated by a prolonged inhomogeneous electric field can be observed for weeks after this field has ceased to be applied. The sample as a whole does not have to be polarized perpendicularly to the ferroelectric axis in order for the above phenomena to be visible.
4. Two mechanisms, that is the nucleation of small frozen regions and the growth of such nuclei, are assumed to be responsible for a gradual hysteresis loop suppression during the prolonged inhomogeneous electric field application.

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