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Investigations of the reduced polarization of triglycine sulphate (TGS) in an electric field perpendicular to the ferroelectric axis

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Abstract. A considerable reduction in the remanent polarization was observed during hysteresis loop measurements on TGS samples previously placed in a constant electric field $E_\perp$ not parallel to the ferroelectric axis $\boldsymbol{b}$. The quasi-stable states of the crystals obtained by means of the application of the field $E_\perp$ were destroyed by prolonged application of an alternating electric field parallel to the b-axis and by annealing above the critical temperature.

1. Introduction

Ferroelectric triglycine sulphate (TGS) undergoes a continuous ferroelectric phase transition at temperature $T_c \simeq 322.2$ K [1]. The dielectric properties of TGS crystals have been investigated in many papers. However, to our knowledge, there are few works concerning the influence of the electric field $E_\perp$ perpendicular to the ferroelectric axis $\boldsymbol{b}$ on these properties [2–4].

As follows from [3], the higher the field $E_\perp$ applied to the TGS crystal, the lower the spontaneous polarization values measured. However, it was an unknown experimental fact whether such a polarization reduction depended on the duration of the application of the field $E_\perp$. Furthermore, quasi-stable states of the crystal can be observed as a result of prolonged application of a field $E_\perp$. Such states may persist after this field has ceased to be applied. The consequences of the application of a field $E_\perp$ are completely different to those observed for $\boldsymbol{E} \parallel \boldsymbol{b}$.

2. Experimental procedure and results

We show the results of the polarization measurements for TGS samples previously placed in an electric field $E_\perp$ not parallel to the ferroelectric axis. A Sawyer–Tower (S–T) circuit with an HP 54600B oscilloscope has been used. The frequency of the driving field E_d was 50 Hz.

The first crystal (sample I) that we have used was cut perpendicularly to the b- and c-axes in the Hoshino–Okaya–Pepinsky coordinate system [5]. The sample, in the form of a perpendicular parallelepiped of dimensions 10.5 mm × 5.7 mm × 5.7 mm, is shown in figure 1. At the beginning, the crystal was annealed without electrodes at 85 °C for about 48 hours. Then the silver paste electrodes, called ‘field electrodes’, were attached to it as in figure 1(a). Next,

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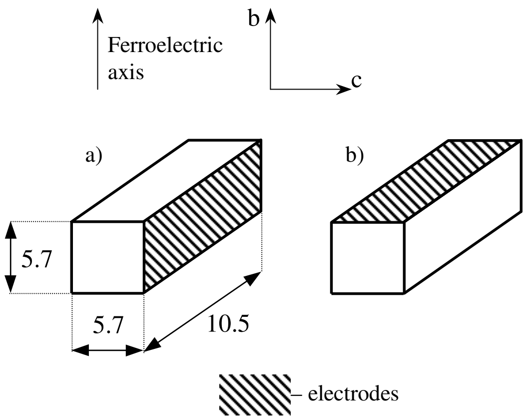


Figure 1. Sample–electrode systems with the field electrodes (a) and with measurement electrodes (b); the dimensions of the sample are given in mm.

the constant electric field $E_\perp$ was applied along the c-axis for 113 hours, at room temperature. The voltage connected to the field electrodes was then equal to 1000 V. Afterwards, the silver electrodes were washed off and the new ones—called below 'measurement electrodes'—attached as in figure 1(b). In this manner, about 20 minutes after the field $E_\perp$ was switched off, the driving electric field could be applied at $t = t_0 = 0$, parallel to the ferroelectric b-axis. Then the hysteresis loop measurements were carried out by means of the S–T method.

The field E_d was initially applied from t_0 to $t_1 \backsimeq 213$ h. The driving voltage amplitude was $U_m = 325$ V. It can be seen in figure 2 that considerable (even 95%) reductions of the original remanent polarization P_{r0} have been observed just after the field $E_\perp$ was switched off.

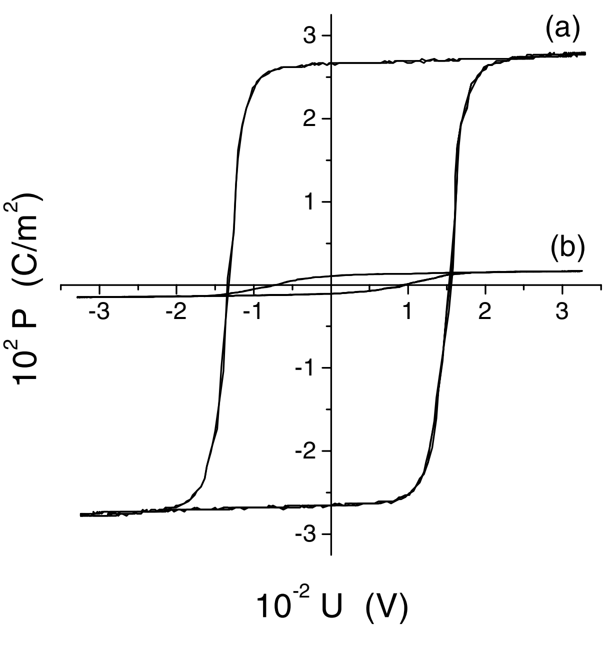
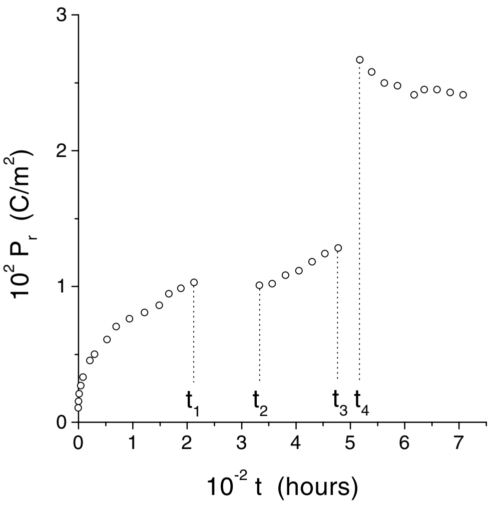
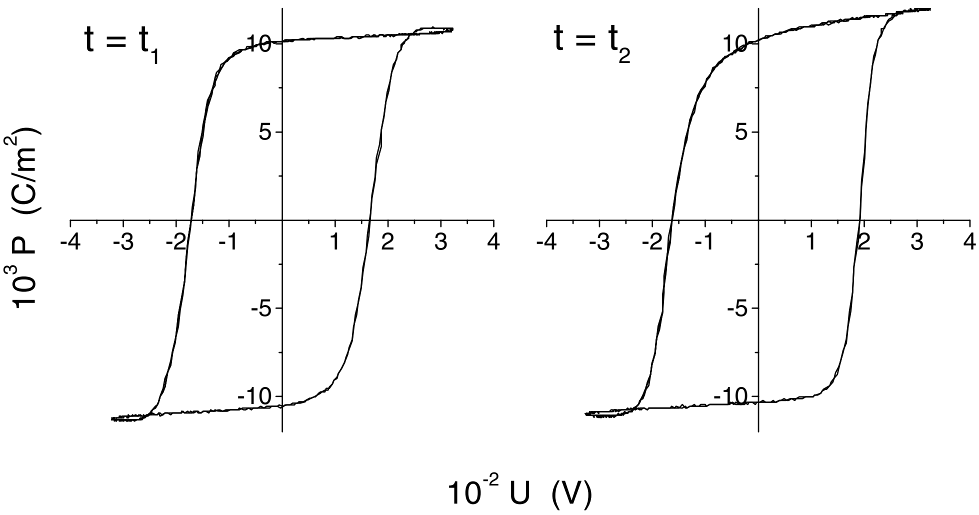


Figure 2. Hysteresis loops obtained before application of the constant field $E_\perp$ ($U = 1000$ V for 113 hours) (a) and after it has been switched off, i.e. three minutes after the driving field has been switched on (b).

The loop (a) obtained for the original sample is much higher than that (b) measured after the $E_\perp$-field was switched off (i.e. three minutes after the field E_d was switched on). However, as can be seen in figure 3(a), the reduced remanent polarization P_r increases with time due to the action of the driving field E_d. Such rejuvenation is most effective for small P_r.



(a)



(b)

Figure 3. The dependence on time t of the remanent polarization P_r measured after the application of the field $E_\perp$ ((a); see the text) and the hysteresis loops measured at t_1 and t_2 (b); the driving field was switched on at $t = t_0 = 0$ and switched off for $t_1 < t < t_2$ and during the annealing at 85 °C for $t_3 < t < t_4$; P_r has been measured with the accuracy of 10^{-4} C m^{-2}.

In the absence of the field E_d, i.e. between t_1 and t_2 when E_d was switched off, the polarization restoration was not visible. In figure 3(b), the values of P_r for both loops measured at t_1 and t_2 are the same. This is a very interesting result, because the time interval $\Delta t = t_2 - t_1$ exceeds 120 hours! However, it has also been found that the loop obtained at t_2 had become somewhat asymmetric in the absence of E_d. The conclusion is that the stable state of such a crystal can be described by a double-well free energy with inequivalent minima. We have not observed any symmetric loop at this stage of rejuvenation.

For $t > t_2$ the driving field was applied and the slow polarization restoration could be observed again. From $t_3 = 478$ h to $t_4 = 518$ h the crystal was annealed at 85 °C for about 40 h (not connected to the S–T circuit). Next, the sample was cooled again to room temperature and the measurements were continued. It has become apparent that, within the limits of the experimental errors, the polarization retrieved the value $P_{r0} \backsimeq 0.027$ C m^{-2}, i.e. that measured before the application of the field $E_\perp$. However, a slight decrease of P_r was observed upon annealing, for $t > t_4$.

The results shown in figure 3 were obtained as the driving field was continuously applied. We found, however, that the reduced remanent polarization of TGS crystal remains almost unchanged in the absence of this field. In figure 4, the values of the mean polarization (the average of the positive and negative remanent polarization values) are shown. The driving field was then applied only during the hysteresis loop measurement, i.e. a few sine-wave cycles were used each time. The result in figure 4 was obtained for the second crystal (sample II, of the same dimensions as in figure 1) previously placed in the field $E_\perp$ ($U = 1000$ V) for about 329 hours. It is apparent that the small reduced polarization increases very slowly with time. Such a rejuvenation may be due to the application of the driving field during the individual hysteresis loop measurements. The extremely reduced loops are usually asymmetric and often narrowed in the middle.

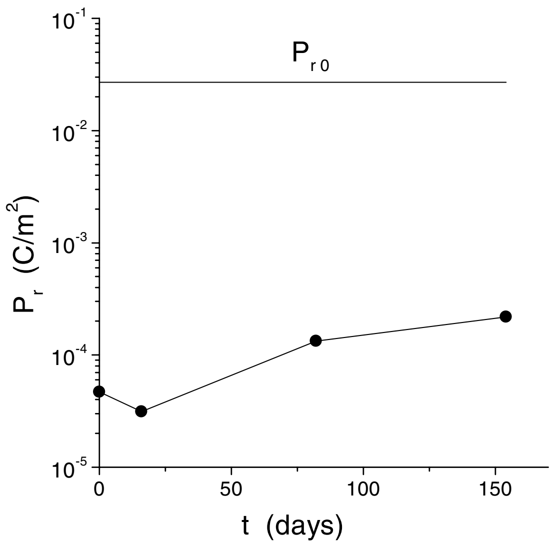


Figure 4. The values of the mean remanent polarization (the average of the positive and negative remanent polarization values) for the sample previously placed in the field $E_\perp \approx 175$ kV m^{-1} for 329 hours, observed at various times after the field $E_\perp$ has been switched off; a few sine-wave cycles of the driving field were applied just during the loop measurements.

It has also been observed that the polarization of the TGS sample previously placed in the field $E_\perp$ for a few days could not be restored by a constant electric field $E_\parallel$ applied parallel to the ferroelectric axis. As an example, in figure 5 the hysteresis loops measured after constant application of fields $E_\perp$ and $E_\parallel$ are presented for the third sample (sample III, of the same dimensions as in figure 1). These results were obtained in the following experiments: at the

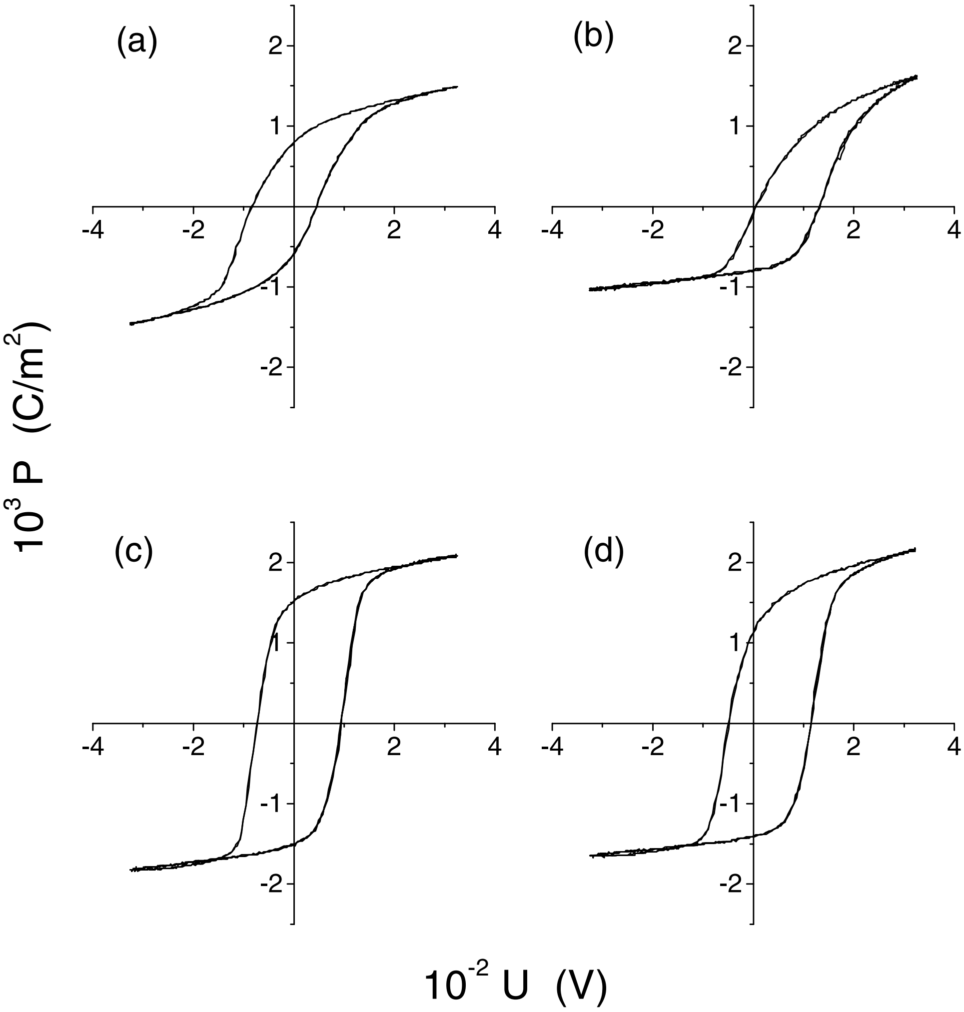


Figure 5. The hysteresis loops obtained when the constant field $E_\perp$ ($U = 1000$ V) was applied for 96 hours: just after the field $E_\perp$ was switched off and the electrodes replaced (a); after application of a constant field $E_\parallel$ ($U = -300$ V) for one minute (b); after just driving-field action for a further four minutes (c); after further constant application of $E_\parallel$ ($U = -1000$ V) for one minute (d).

beginning, an electric field $E_\perp$ ($U = 1000$ V) was applied for 96 hours to the crystal previously annealed for 50 hours at $T = 90\,^\circ$C. After switching off this field and electrode replacement, the hysteresis loops were measured. The loop (a) in figure 5 was obtained just after the attachment of the measurement electrodes. Afterwards, a constant voltage $U = -300$ V was applied to these electrodes for one minute, so the mean electric field was directed along the b-axis. An asymmetry of the loop (b) measured just after the voltage $U = -300$ V was switched off is visible (a negative sign of U was deduced from the asymmetry of the loop). The next result, obtained after four minutes of application of just the driving S–T field, is shown as the loop (c). The loop (d) relates to the result measured after the further application of the constant voltage $U = -1000$ V to the measurement electrodes for one minute. Like in the case of $U = -300$ V, no significant polarization restoration can be found. Finally, a constant voltage

$U = -1000$ V was applied to the measurement electrodes for 13.66 hours. In figure 6, the asymmetric hysteresis loops measured at various times after this voltage was switched off are shown. In particular, the result of prolonged driving-field action are presented here. On the one hand, the remanent polarization increases and, on the other, the hysteresis loop becomes more and more symmetric.

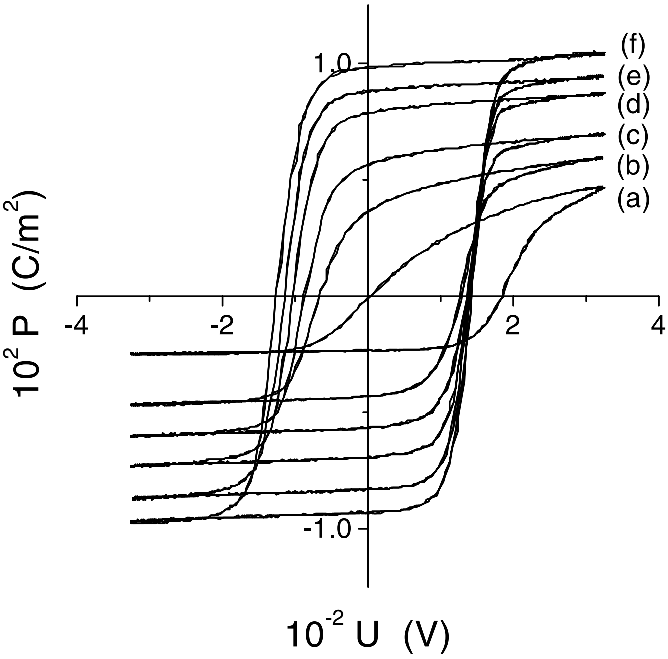


Figure 6. The hysteresis loops obtained upon application of the constant field $E_{\parallel}$ ($U = -1000$ V)—to the sample in the same state as in figure 5(d)—for about 13.66 hours: at $t = 0$ (a), i.e. when the driving field was switched on (a few minutes after the field $E_{\parallel}$ was removed) and at $t = 0.033$ (b), 0.5 (c), 3.5 (d), 10.5 (e) and 22.75 hours (f); a negative sign of U in figures 5 and 6 has been deduced from the asymmetry of the loop.

As follows from figures 5 and 6, the constant electric field parallel to the ferroelectric axis makes the hysteresis loop asymmetric. However, such asymmetry does not disappear instantaneously upon the removal of $E_{\parallel}$, in contradiction to the analogous measurements for the original crystal (not influenced by $E_{\perp}$).

3. Conclusions

The polarization reduction $\Delta P_r = P_r - P_{r0} < 0$ in TGS crystals placed in an electric field $E_{\perp}$ has already been demonstrated in [3]. However, we point out that the value $P_r < P_{r0}$ may be maintained after the field $E_{\perp}$ has been switched off. Then the crystal remains in the quasi-stable state observed in figure 3(a) for $t_1 < t < t_2$ and in figure 4.

The free energies F for different states of the crystal are shown schematically in figure 7. The arrows indicate the results of the application of the fields E_d, $E_{\perp}$ and $E_{\parallel}$, as well as the consequence of the annealing. The induced asymmetry of the two $F(P)$ dependences ((b) and (c)) with minima for $P \ll P_{r0}$ do not disappear spontaneously upon the removal of the corresponding stimulus ($E_{\perp}$ or $E_{\parallel}$). In figure 8, the connection between the experimental data

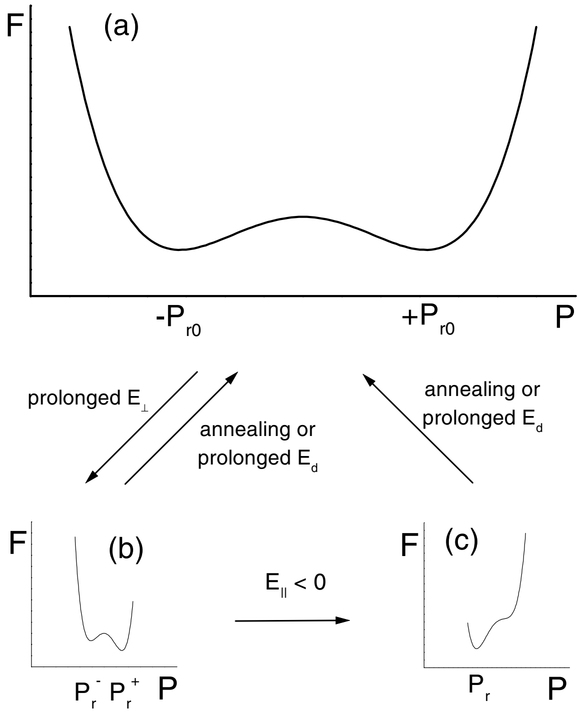


Figure 7. The polarization dependence of the free energy shown schematically: for the original crystal (a) and for the crystal previously placed in the field $E_\perp$ (b) and next in the field $E_\parallel$ (c); the arrows indicate the result of the action of the driving field E_d and the action of constant fields $E_\perp$ and $E_\parallel$, as well as the annealing of the sample.

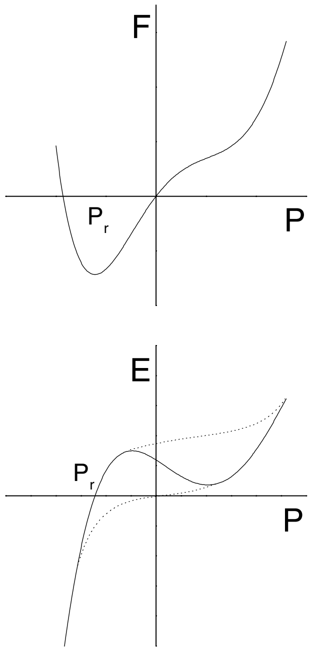


Figure 8. The polarization dependence of the free energy F and the corresponding function $E = \partial F/\partial P$ versus P shown schematically for the crystal with the reduced hysteresis loop, shifted and deformed due to the action of the field $E_\parallel$.

and free-energy minima is presented. As an example, the result of the action of the field $E_\parallel$ is shown. The asymmetry in $F(P)$ that appeared as a result of the application of $E_\parallel$ does not disappear instantaneously when this field is switched off. Such behaviour is quite different from that of the original TGS crystal.

It is an interesting fact that we have found no method of instantaneously restoring the original properties of the crystals previously placed in the field $E_\perp$. Transitory increase of the Sawyer–Tower driving-field amplitude even up to 250 kV m^{-1} $\approx 5E_{co}$ does not change the remanent polarization of the crystal (where E_{co} is the coercive-field value). In figure 9, the result of the application of a driving field with this high an amplitude for one minute has been shown. Only prolonged application of the alternating field enhances the remanent polarization as in figure 3(a). On the basis of our investigations, we can state that the most effective method of restoring the original remanent polarization is annealing the sample above the Curie temperature, as is also visible in this figure.

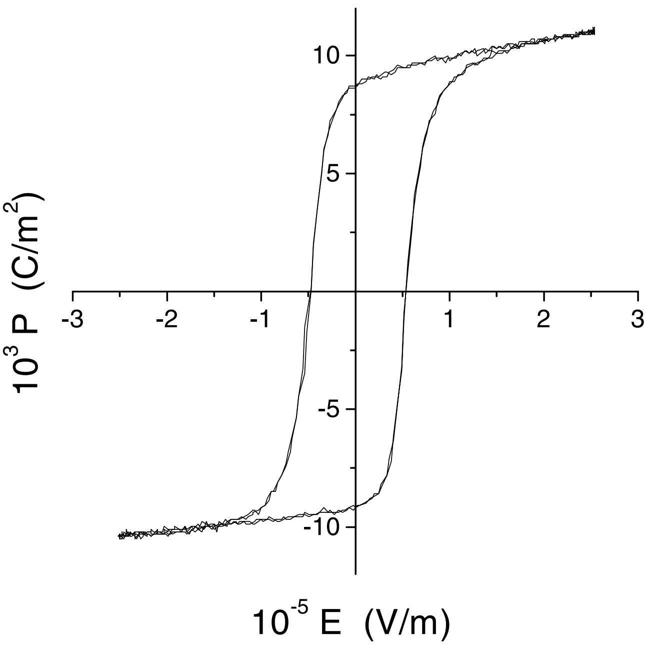


Figure 9. The hysteresis loop observed for TGS crystal b-plate for the driving-field amplitude of 250 kV m^{-1}; the result was obtained after one minute of this field action; the crystal plate (sample IV), of dimensions 5.6 mm × 1.98 mm × 5.7 mm, was cut out from the perpendicular parallelepiped after the switching off of the field $E_\perp = 175$ kV m^{-1}, previously applied for 149 hours.

The fact of the occurrence of the prolonged polarization restoration process at $E_d \neq 0$ seems to confirm the assumption made in [6] that the electric charge-transport contribution should be taken into account when interpreting experimental data obtained with a field $E_\perp$ parallel to the c-axis. The electric conductivity is especially high just along this direction [7]. Furthermore, a particular anti-parallel domain structure may be formed here and there in the crystal in the field $E_\perp$. Such a structure can be stabilized by charged particles whose diffusion through the crystal is expected to take rather a long time. Exactly this process seems to be the origin of the slow relaxation phenomena observed in our experiments. The small remanent polarization may then be treated as a result of the clamping of the anti-parallel domains (cf. [8]).

The question arises of whether the quasi-stable states originated by the field $E_\perp$ may also be observed in the paraelectric phase. In [6], susceptibility data have been published for TGS samples placed in a field $E_\perp$. Contrary to the case for the results of the present paper, this field was applied continuously during the measurements. A two-pair electrode system was used there. Although a very slow relaxation process was found even above T_c, the susceptibility data in [6] could not be treated as evidence of some kind of quasi-stable state. As follows from the results of the present work, a strong rejuvenation takes place during the annealing above the Curie temperature. Consequently, there is no reason for there to be any permanent state different from that of the original sample, in the paraelectric phase. Moreover, the extremely slow relaxation process, observed just above T_c in [6], suggests a correlation between the occurrence of quasi-stable states and the ferroelectric ordering.

The results shown in the present paper concern the behaviour of TGS crystals previously placed in an electric field perpendicular to the ferroelectric axis. The influence of such a field is completely different to that of a parallel one. In particular, the dielectric properties of TGS crystals remain changed after the field $E_\perp$ has been switched off. Some examples have been presented in this paper. However, we suppose that many other unexpected properties will be found and investigated in the future.

Acknowledgments

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