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# The transverse field effect in the triglycine sulphate ferroelectric

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#### Abstract

The thermodynamic state of a triglycine sulphate crystal, previously exposed to an electric field parallel to the non-ferroelectric c-axis, has been investigated. The frozen ferroelectric c-domains have been observed by a liquid crystal technique and under the scanning electron microscope. Pyroelectric properties and polarization in the non-ferroelectric direction have been investigated. Regions of dipoles that are strongly correlated along the c-direction as well as the clamping of the b-polarization switching have been found to be accompanied by permanent transverse polarization.

# 1. Introduction

The influence of an electric field  $E_{\parallel}$  parallel to the ferroelectric axis on dielectric properties of uniaxial ferroelectrics has been investigated in many papers (e.g. [1–5]). Strongly fielddependent electric susceptibility values were measured close to the critical point. In the ferroelectric phase a single-domain (or almost single-domain) state of a crystal placed in such a field could be easily reached. However, after the longitudinal electric field disconnection more and more domains with polarization vectors of opposite senses appeared and electric susceptibility could not be treated as a stationary parameter for a long time. The crystal tended very slowly to its equilibrium thermodynamic state. Its domain structure and other dielectric properties were then very sensitive to application of even a small field  $E_{\parallel}$ . The conclusion arises that the changes caused by the electric field parallel to the ferroelectric axis are not permanent. After this field disconnection the system rather tends to random arrangement of opposite polarized regions (domains).

The situation is quite different in the case of the transverse electric field. The results of investigations of dielectric properties of triglycine sulphate (TGS) crystals in an electric field  $E_{\perp}$  perpendicular to the ferroelectric axis *b* have been reported in a few papers, e.g. in [6, 7].

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**Figure 1.** The comparison of domain structures at room temperature: for the original (rejuvenated) TGS sample [12] (a) and for another TGS sample after prolonged constant transverse electric field  $(E_{\perp} \parallel c, |E_{\perp}| = 444.5 \text{ kV m}^{-1})$  application for 120 h (b); in both cases the  $P_{\parallel}$  component of polarization is perpendicular to the figure plane.

Besides, the measurements of an electric current flowing along various crystallographic directions were carried out [8, 9]. Then, an electric field not parallel to the ferroelectric axis was also applied.

Until recently, both fields  $E_{\parallel}$  and  $E_{\perp}$  were treated similarly, i.e. all qualitative changes caused by them were assumed to disappear instantaneously or gradually in zero electric field. We found out [10–14], however, that the transverse electric field  $E_{\perp}$  may permanently (although reversibly) change some dielectric properties of TGS. After application of a constant electric field perpendicular to the ferroelectric *b*-axis, a considerably reduced hysteresis loop or even its disappearance was observed below the Curie temperature. The suppression of low frequency dispersion also took place in this case. Although these new properties might persist for a long time after the field  $E_{\perp}$  was switched off, the original ones could be easily restored by annealing above the critical temperature. The results mentioned above have been presented in [10–14] and are not discussed in detail in the present paper. Below, we show that they are connected with the appearance of a transverse polarization in the sample. It seems to be an interesting experimental result because the TGS crystal is still treated as a uniaxial ferroelectric. The results concerning the domain structure and pyroelectric properties of crystals formerly exposed to the electric field parallel to the c-axis (in the coordinate system given in [15]) are presented. Such a direction has been chosen because many physical effects in TGS are visible especially while observed just along this axis. The experiments under uniaxial pressure [16], conductivity measurements [8, 9] and our results [10] can be mentioned here, for example. We have called the phenomenon described in the present paper the transverse field effect.

# 2. Experiment

#### 2.1. Domain structure

The constant electric field  $E_{\perp} \parallel c$  has also been found to be the origin of quite a new frozen c-domain structure. The cross-section of the TGS crystal, previously exposed to the field  $E_{\perp}$ , is shown in figure 1(b). The light and dark stripes, parallel to the c-axis, correspond to three-dimensional regions of opposite values of the longitudinal polarization component  $P_{\parallel} \parallel b$ , where b (b-axis) is perpendicular to the figure plane. It is visible that the c-domain walls are perpendicular to those of the original (not influenced by  $E_{\perp}$ ) or rejuvenated TGS crystal



**Figure 2.** The still frozen (after the transverse electric field disconnection) domain structure observed after the sinusoidal driving electric field (of amplitude of the order of  $10^5$  V m<sup>-1</sup> and frequency 50 Hz) action for 28 h, at room temperature; the  $P_{\parallel}$  component of polarization is perpendicular to the figure plane.



Figure 3. The frozen *c*-domains observed under the electron microscope at room temperature; the  $P_{\parallel}$  component of polarization is perpendicular to the figure plane.

(figure 1(a), [12]). Such a new frozen structure does not disappear after the transverse field has ceased to be applied. Moreover, it cannot be easily destroyed by an alternating driving field similar to that used in the Sawyer–Tower method or by a constant electric field, both parallel to the *b*-axis. In figure 2, the rigid *c*-domains observed after 28 h of the sinusoidal driving field (of amplitude of the order of  $10^5$  V m<sup>-1</sup> and frequency 50 Hz) action are shown. The light and dark regions appearing due to the opposite values of  $P_{\parallel}$  still remain easily visible. To restore the original dielectric properties this field would have to be applied for a few hundred hours [11]. The photographs in figures 1 and 2 were taken using the liquid crystal technique. The surfaces of samples (cleavage *b*-planes) were then covered with the thin film of a nematic liquid crystal so the light and dark regions corresponded to the opposite directions of the polarization component  $P_{\parallel}$  along the ferroelectric axis *b* (perpendicular to the figures' planes).

The *c*-domain structures have been observed by the liquid crystal and etching techniques as well as under the scanning electron microscope (figure 3). The light and dark stripes in figure 3 appeared due to twofold interactions between electrons and differently charged regions that arose on the crystal surface as a consequence of the discontinuity in  $P_{\parallel} > 0$  or  $P_{\parallel} < 0$ 

values of  $P_{\parallel}$ . Such striations did not disappear even after polishing with fine-grained emery paper and wet silk so they could not be treated as any structural or morphological features of the crystal. The domain structure shown in figure 3 confirms the results obtained by the liquid crystal method, presented in figures 1 and 2.

The new rigid c-domains do appear in the whole volume of the crystal. After dividing the TGS b-plate (previously cut out of the perpendicular parallelepiped influenced by a transverse field) into two thinner ones, the same frozen domain motifs—but the mirror reflections—can be observed on both internal surfaces. The TGS crystals previously exposed to the transverse field may be divided into smaller ones without any change of their new dielectric properties. The domain stripes are sometimes a few millimetres long (i.e. as long as a sample) and their width values lie between about 0.01 and 1 mm. So far, we have not managed to find any evidence indicating that the dimension of the rigid domain along the b-axis direction is larger than 1 mm. Such domains seem to be three-dimensional oblong objects stretching along the c-axis. Their sections can be visible as dark and light stripes on the b-plate surface of the crystal.

#### 2.2. Pyroelectric properties

Investigations of a depolarization electric current flowing along the *b*-and *c*-directions were carried out. For the electric current density measurements the Keithley 6517A electrometer was used. All investigations were carried out in an atmosphere of nitrogen. Because of the shape and thickness of the samples only two rectangular silver paste electrodes (without any guard ring) were used. The rejuvenated (annealed in the paraelectric phase) TGS crystal in the form of a perpendicular parallelepiped (5.7 mm × 5.7 mm × 10.4 mm, along *b*, *c*, *b* × *c*, respectively) was used in each experiment described below.

The results of the measurements of density of the short-circuit electric current  $J_2$  flowing along the ferroelectric *b*-axis (called *b*-current density) are shown in figure 4(a). The constant rate of temperature change was 1 K/25 min. Curve I concerns the temperature dependence obtained for the original sample (rejuvenated and not influenced by  $E_{\perp}$ ). The density of the electric *b*-current measured for the crystal previously exposed (at room temperature, after rejuvenation) to the electric field  $E = 351 \,\mathrm{kV} \,\mathrm{m}^{-1}$  parallel to the *c*-axis for 166 hours is shown as dependence II. The corresponding polarization data obtained as a result of the numerical time integration are presented in figure 4(b). In both cases (I and II), just before *b*-current measurements, the crystal was polarized in the field  $E = 175 \text{ kV m}^{-1}$  directed along the baxis for an hour. As follows from figure 4, only in the case of the original sample (rejuvenated, not exposed to  $E_{\perp}$ ) was a single-domain state reached in this way. The polarization then took classical values from about 0.03 C m<sup>-2</sup> at room temperature to zero at the critical point. On the other hand, the rigid *c*-domains previously appearing as a result of the prolonged transverse field action could not be reversed by a constant electric field  $E \parallel b$ . Therefore a rather small pyroelectric current was observed in case II. Such behaviour is in agreement with the data obtained during the hysteresis loop measurements [13].

Because the transverse field effect was caused by the prolonged electric field perpendicular to the ferroelectric axis, the possibility of the appearance of polarization perpendicular to this axis was considered. The crystal was exposed to the constant transverse electric field  $E_{\perp} \parallel c$   $(E_{\perp} = 175 \text{ kV m}^{-1})$  for  $t_f = 24$  h, at various temperatures  $T_n$  (n = 1, 2, ..., 8). For  $T_1$ , the corresponding measurements were also carried out for  $t_f = 2$  and 16 h, for comparison. After the field was switched off, a short-circuited electric current of density  $J_3$  was detected along the *c*-axis at the constant temperature  $T_n$  for a few hours. During this time an exponential decay of  $J_3$  was observed. When the current density reached a rather steady and small value,



**Figure 4.** The temperature dependence of the *b*-current density  $J_2$  (a, enlargement in inset) and *b*-polarization  $P_{\parallel}$  (b) obtained in heating for the original crystal (I) and for the crystal previously exposed to the electric field  $E_{\perp}$  parallel to the *c*-axis (II); just before the current density measurements (for both initial states of the crystal) the sample was polarized (in  $E_{\parallel} = 175 \text{ kV m}^{-1}$ ) along the ferroelectric *b*-direction for an hour (see the text).

measurements of the density  $J_3$  as a function of temperature T were carried out during the heating between  $T_n$  and 338 K. The temperature was changed linearly at the rate of 1 K/25 min in each case. Significant charge transport is observed along the *c*-direction, especially close to the critical temperature  $T_c = 322.2$  K (figure 5). The sense of the depolarization *c*-current density vectors  $J_3$  (both at the constant temperature  $T_n$  and during the heating) was opposite to that measured during the *c*-polarization process, i.e. when the transverse field was applied. It should be stressed that the maxima of the electric current density shown in figure 5(a) can be observed at  $T_c$  only after the transverse field application at the temperature  $T_n \leq T_c$ . If the temperature is increased above  $T_c$  the 'frozen' sample will lose its new properties. For this reason, during the repeated measurements carried out in the heating from the same  $T_n$  up to above  $T_c$  no maximum  $J_3(T)$  is detected at  $T_c$  (the electric current density is practically equal to zero in the whole region between  $T_n$  and 338 K). To observe such an extremum again the repeated application of the transverse field in the ferroelectric phase is required.



**Figure 5.** The temperature dependences of the *c*-current density observed after the prolonged electric field  $E_{\perp} = 175 \text{ kV m}^{-1}$  application in the *c*-direction for  $t_f = 24$  h at various temperatures  $T_n$  (n = 1, 2, 3, 5) and the comparison for  $t_f = 2$ , 16 and 24 h at  $T_1$  (a); the comparison of two dependences, see the text (b); the  $P_3(T)$  dependences of the crystal previously polarized in  $E_{\perp} = 175 \text{ k V m}^{-1}$  at T = 299.7 K (then heated) and at  $T_A = 314.3 \text{ K}$  (then cooled and heated) (c); the  $P_3(T)$  dependences for n = 1 and 2 (d).

#### 3. Discussion

# 3.1. Clamping of switching process

The switching of the polarization  $P_2$  in the original TGS crystal is caused by the libration of *glycine I* ion (NH<sub>3</sub><sup>+</sup>CH<sub>2</sub>COOH) as a whole together with simultaneous flipping of the NH<sub>3</sub><sup>+</sup> molecule through the CH<sub>2</sub>COOH plane [17]. Then we deal with the transition of *glycine I* from its state shown in figure 6(a) to another one drawn in figure 6(b). Because of the rotation of hydrogen atoms in the NH<sub>3</sub><sup>+</sup> ion of *glycine I* [18] no permanent hydrogen bond with SO<sub>4</sub><sup>2-</sup>



Figure 6. Two states of the *glicyne I* molecule corresponding to the two senses of longitudinal polarization vector; the rotating  $NH_3^+$  groups have been drawn schematically.

can be expected here. For this reason the NH<sub>3</sub><sup>+</sup> group of the *glycine I* freely changes its position. However, the motion of the NH<sub>3</sub> group seems to be permanently hindered as a result of the prolonged transverse field action. Consequently, no switching of  $P_2$  can take place even in the field of 175 kV m<sup>-1</sup>, as in the case of the data in figure 4(a), where no single-domain sample could be obtained at room temperature. For comparison, the coercive field for the original TGS sample is equal to about 25 kV m<sup>-1</sup>, at the same temperature. Frozen dipoles cannot be reoriented in an alternating electric field similar to that used in the classical Sawyer–Tower method, either, which is shown in figure 2.

#### 3.2. Transverse polarization

The experimental facts given below enable us to ascertain that the clamping of  $P_{\parallel}$  is accompanied by an appearance of a dipole transverse polarization  $P_{\perp}$  ( $P_{\perp} = |P_{\perp}|$ ). The motion of free electric carriers released from *c*-electrodes during the heating of the crystal after the transverse field action can be considered as a pyroelectric *c*-current, flowing perpendicularly to the ferroelectric axis. The areas under  $J_3(T)$  experimental functions for n = 1, 2, 3 and 5 (figure 5(a)) correspond to the values  $P_3(T)$  generated by  $E_{\perp} = 175$  kV m<sup>-1</sup> applied for  $t_f = 24$  h at various temperatures  $T_n$  (connected by dotted line, for n = 1, ..., 8, in figure 5(d)).

In our opinion, the transverse polarization appears as a result of a special molecular arrangement. The fraction of permanently reoriented dipoles then occupies new metastable states with  $P_{\perp} \neq 0$ , schematically shown in figure 7(a). Just these dipoles form rigid *c*-domains which can be visible here and there in the crystal previously exposed to the transverse electric field. As follows from figures 5(c) and (d), the value of  $P_3$ , being the investigated component of  $P_{\perp}$ , is only about three to four times lower than that of spontaneous  $P_2$ , at room temperature. This is an unexpected result because the TGS crystal is still treated as a uniaxial ferroelectric.

In figure 5(c), the evidence is given that dipoles are actually permanently reoriented by the field  $E_{\perp} = E_3$ . The transverse field  $E_3 = 175 \text{ kV m}^{-1}$  was applied to the crystal for 24 h at  $T_A = 314.3$  K. After this field switching off, the temperature dependence of  $P_3$  has been



**Figure 7.** Stable and metastable states occupied by dipoles; inset, the reorientation of polarization vector in  $E_{\perp}$  (a); the TGS crystal in the shape of a cube and projections of the  $P' = P'_2 + P_3$  vector onto the sample surfaces, drawn schematically; the dashed vector concerns the domain with negative  $P'_3$ ; presumed orientation of the domain wall is shown (b); not to scale.

measured while cooling the crystal to about 300 K and then heating it up to above  $T_c$ . The polarization values obtained in both cases coincide. Small differences are, in our opinion, due to the numerical integration of a current density which should be treated as a background effect not connected with the *c*-polarization. The most interesting is that the value of  $P_3$  appearing at  $T_A$  could be enhanced only by cooling the crystal. No external fields were then required. This means that the transverse polarization can spontaneously change its value due to the reorientation of dipoles occupying their new metastable states. Such a motion seems to correspond to a shift in the  $P_{\perp}$ -coordinate of the local minimum for  $P_{\perp} \neq 0$ , shown in figure 7. The molecules cannot overcome an energy barrier provided that the crystal is not heated above  $T_A$ .

In figure 5(b), two  $J_3(T)$ -dependences, both measured in heating, are compared. One of them (solid line) has been replotted from figure 5(a) (for  $T_1, t_f = 24$  h). The second dependence (circles) consists of two parts: for T < T' and T > T''. The crystal was then heated up to T' and kept at this temperature for several hours. Next, the heating process was continued but between T' and T'' the measurement circuit was opened and no current could be measured then. For T < T' both dependences coincide very well. As shown, however, the current density (circles) falls instantaneously to zero as soon as the temperature ceases to be increased at T'. About one degree above T'' both dependences coincide again. Such a result confirms the statement that the dipole transverse polarization can actually appear in the crystal

exposed to the prolonged field  $E_{\perp}$ . Otherwise, e.g. in the case of space-charge polarization, quite a different temperature dependence  $J_3(T)$  would be expected above T''. It should be also stressed that the presented experimental results are very well reproducible, which would be rather strange in the case of polarization appearing due to randomly distributed free charges.

## 3.3. The role of free electric carriers

New stripelike domains seem to be stabilized by free electric carriers flowing into the crystal and trapped there during the transverse field application [19]. Such a suggestion can be justified by the fact that the formation of a new rigid c-domain structure turns out to be a rather long-time process. Moreover, we have observed that the freezing of new domains does not vanish even after the temporary heating of the crystal up to above the critical temperature. This means that c-domains may survive just above the Curie temperature, probably being stabilized by internal fields originated by free electric carriers still remaining inside the crystal (cf [20]). Also a suppression and a temperature shift in the susceptibility maximum [14] observed in the heating lead us to suppose that the released dipoles are then influenced by internal fields originated by the trapped free electric carriers, remaining even in the paraelectric phase. The transverse field effect, however, cannot be understood as that observed due to the enhanced concentration of the trapped electric carriers, i.e. as the macroscopic polarization of the space charge. As follows from our observation of single-domain *b*-plates under the polarizing microscope, after an hour of the  $E_{\perp} \parallel c$  field application, small domains of the opposite  $P_{\parallel}$  start to be visible as narrow and short stripes directed along the *c*-axis. No regions close to electrodes are favoured, as might be expected in the case of space-charge polarization. Domains appear randomly here and there in the crystal. Becoming larger and larger they form a frozen stripelike structure in the course of time.

#### 3.4. Charging process

At a constant temperature the polarization  $P_{\perp}$  increases with time during the transverse field  $E_{\perp}$  application to the rejuvenated crystal. The dipoles gradually leave their original states with  $P_{\perp} = 0$  and become confined in their new reoriented positions with  $P_{\perp} \neq 0$ . This is rather a long process and  $P_{\perp}$ -values depend on the time  $t_f$  of the transverse field application. As follows from figure 5(a) (top diagram) the time of  $t_f = 24$  h chosen by us corresponds to the saturated values of  $P_{\perp}$ . The data obtained after  $t_f = 16$  and 24 h coincide very well. On the other hand, much smaller transverse polarization can be generated after  $t_f = 2$  h. The conclusion arises that the number N of switchable dipoles tends to zero when the crystal is exposed to the field  $E_{\perp}$  for several hours.

A slightly different result can be obtained from the Sawyer–Tower type hysteresis loop measurements. As follows from our data [13], the time dependence N(t) can be then approximately described by the formula

$$N = N(t) = N_0 \mathrm{e}^{-t/\tau} \tag{1}$$

where t is the time of the transverse field application and  $N_0 = N(0)$ . For a given temperature, the relation  $N \sim P_r$  (i.e.  $N/N_0 \approx P_r/P_{r0}$ ) is assumed where  $P_r = (|P_r^+|+|P_r^-|)/2$  is the mean remanent polarization,  $P_{r0}$  the remanent polarization for t = 0 and  $P_r^+$  and  $P_r^-$  are positive and negative values of the remanent polarization, respectively. The relaxation time  $\tau$  is here equal to 36.8 h. The time dependence of N is shown in figure 8, where the solid line represents equation (1). The corresponding hysteresis loops have been added in the inset. The hysteresis loop parameters  $P_r^+$  and  $P_r^-$  could be obtained because the transverse field was disconnected



**Figure 8.** The time dependence of  $N/N_0 \approx P_r/P_{r0}$  during the transverse electric field  $E_{\perp} \parallel c$  application at room temperature; the solid line represents equation (3) for  $\tau = 36.8$  h as the least squares fit; inset, the corresponding hysteresis loops (after [13]).

once in a while for about 8 min. Then the sample was reconfigured in order that the remanent polarization values were measured (see [13]).

A quantitative difference between the data obtained from hysteresis loop and electric current density measurements may follow from the fact that the crystal is rejuvenated by an alternating field. Such destruction makes the freezing process more difficult. The results drawn from comparing both types of measurement have been published [21].

#### 3.5. Domain walls

The appearance of the transverse polarization leads us to suppose that a new type of domain wall may appear in the frozen TGS crystal. In figure 7(b), the projections of the polarization vector  $P' = P'_2 + P_3$  (cf figure 7(a)) onto three surfaces of the sample cube, perpendicular to the  $a^*$ -, b-and c-directions, have been shown, where the  $a^*$ -axis is perpendicular to both b-and c-axes of the monoclinic system. The dashed line represents the polarization vector in the domain with  $P'_2 < 0$  so that it is visible that domain walls are not here of 180° type.

# 3.6. Rejuvenation

The number N' of still frozen glycine molecules as well as transverse polarization values are determined by the value of the potential barrier, by the position of the metastable state minimum (figure 7(a)) and by the density of trapped free electric carriers. The dotted line in figure 5(d) represents the maximal transverse polarization values  $P_3$  reached in the field  $E_3 = 175$  kV m<sup>-1</sup> applied for 24 h at various temperatures. The frozen system of dipoles appearing in this way is stabilized by free electric carriers. The glycine I molecules occupy their metastable states shown in figure 7(a). The potential barrier decreases just close to the critical point  $T_c = 322.2$  K and, consequently, the transverse 'susceptibility' ( $\sim P_3(T)$ , dotted curve in figure 5(d)) dramatically falls to zero. Then a 'softening' of the system is observed.

As shown in figure 5(c), during heating of the formerly frozen TGS crystal from  $T_n$  up to  $T_c$  the transverse polarization decreases. Many various, but highly reproducible  $P_3^{(n)}(T)$ -dependences can be observed in figure 5(d). All of the  $P_3^{(n)}(T)$ -curves lie under the dotted line because more and more dipoles are thermally activated and they return from the states with

 $P_{\perp} \neq 0$  to the original ones with  $P_{\perp} = 0$  (figure 7(a)). The system then tends to a stationary state described by the following relation between the numbers *N* and *N'* of activated and still frozen dipoles, respectively:

$$\frac{N}{N'} = \exp\left(\frac{-\Delta H}{kT}\right),\tag{2}$$

where  $\Delta H$  is the activation energy (enthalpy) and k is the Boltzmann constant. Free electric carriers inside the sample, hitherto stabilizing the frozen stripelike domain structure, leave the crystal. The system of dipoles becomes more or less rejuvenated, depending on the temperature it approaches (cf [13]). As shown in figure 4(b), the current density (circles) falls instantaneously to zero as soon as the temperature ceases to be increased at T'.

The question arises of the physical interpretation of the  $\Delta H$ -barrier. As mentioned, after the transverse electric field action dipoles are strongly correlated along the *c*-direction. They form rigid *c*-domains and therefore their individual motion inside is hindered. Free electric carriers trapped during the charging process compensate polarization discontinuities. The glycine molecules frozen in this way exhibit a transverse dipole moment, permanently induced by  $E_{\perp}$ . On the other hand, a clamping of the switching process along the ferroelectric *b*-axis is observed. Consequently, the individual molecules can be considered as those confined in the potential well. To overcome the  $\Delta H$ -barrier means making the frozen system softer. Such a softening can be easily reached by heat treatment and the  $\Delta H$  corresponds to the required heat transfer per dipole in the domain. For this reason formula (2) can be used. On the other hand, the transverse polarization can spontaneously vary with temperature as a consequence of a collective reorientation within a given domain, which corresponds to a shift in the  $P_3$ coordinate of the metastable state minimum in figure 7(a). Some thermally induced changes in size of such a domain cannot be excluded, either.

## 4. Summary

After an application of a transverse electric field, quite new permanent dielectric properties of the TGS crystal are observed. A strong correlation along the non-ferroelectric *c*-axis is accompanied by the frozen transverse polarization  $P_3$  with a value of the same order as that of spontaneous  $P_2$ . The switching process along the ferroelectric *b*-axis is fully clamped. Quite a new orientation of domain walls is then favoured. The wall normal is parallel to the  $b \times c$ -direction, not to the *c*-axis, as in the original TGS crystal. Furthermore, domain walls not of 180° type are expected after the  $E_{\perp}$ -action. The domain wall motion is strongly hindered.

During the first heating from the ferroelectric phase up to the paraelectric one, following the transverse field application below  $T_c$ , a pyroelectric current can be measured along the non-ferroelectric *c*-axis. On the other hand, a considerable suppression of *b*-current is observed (in a frozen polydomain state). The effects mentioned above, observed after the transverse field has ceased to be applied, are not the results of any crystal damage, because original properties can be easily restored by annealing above the Curie temperature.

In our opinion, quite a new permanent arrangement of dipoles—giving rise to  $P_3 \neq 0$ —is actually responsible for such behaviour. Although a system of domains is rigid at a given temperature, the orientation of frozen dipoles can be collectively changed by heat treatment. Then various temperature dependences both of  $P_{\parallel}$  and  $P_{\perp}$  polarization values can be generated in this way. Most interestingly, the transverse polarization can rise spontaneously, i.e. as a result of only cooling a crystal. On the other hand, during heating, frozen dipoles are being released from metastable states with  $P_3 \neq 0$ . The activation energy (enthalpy) for this process dramatically decreases as temperature tends to  $T_c$ .

Summing up, we can state that the transverse electric field makes the original TGS crystal quite a different material. We suppose that the new dielectric properties induced permanently by this field, i.e. the *c*-domain structure, the new pyroelectric properties, the reduction of the hysteresis loop and the suppression of the low-frequency dispersion, can be observed not only in TGS. Various ferroelectric crystals may be investigated in order to find effects similar to those we have presented in our paper. Because some physical properties could be then permanently changed in a simple manner in  $E_{\perp}$ , the possibilities of their application would be of interest. In particular, pyroelectric properties might be considerably modified. Some interesting results have been already obtained in the ferroelectric Rochelle salt [25]. This fact suggests that we deal with an effect peculiar to a certain group of compounds. The influence of the transverse field on a uniaxial system (ferromagnet) has been theoretically analysed in many papers, e.g. in [26]. The anisotropy of the magnetization correlation function has been discussed there.

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