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The influence of a transverse electric field on the low-frequency dispersion in triglycine sulphate

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Abstract. The thermodynamic state of a triglycine sulphate (TGS) crystal, previously exposed to an electric field E parallel to the c -axis, has been investigated. The temperature dependences of the real part of the electric permittivity and $\tan \delta$ have been measured at various frequencies. It has become apparent that the domain wall oscillation contribution to the dispersion phenomena is then almost completely negligible. Considerable suppression of the dielectric dispersion has been found above 304 K. The possibility of the occurrence of anti-parallel, frozen c -domains in TGS has been confirmed.

1. Introduction

We have recently found [1, 2] that a transverse electric field, i.e. a field perpendicular to the ferroelectric axis, considerably and permanently changes the dielectric properties of triglycine sulphate, $\text{NH}_3^+\text{CH}_2\text{COO}^-(\text{NH}_3^+\text{CH}_2\text{COOH})_2\text{SO}_4^{2-}$ (TGS). For example, reduction or even disappearance of the hysteresis loop, suppression of the susceptibility maximum and its shift towards higher temperatures as well as a quite new frozen, striped c -domain structure have been observed by us; for example, the c -domains shown in figure 1 were obtained after the application of a field $E \parallel c$ of 175 kV m^{-1} for about 50 hours at room temperature. The spontaneous polarization is directed along the b -axis—as in the original TGS crystal—but the domain walls are now parallel to the c -direction, i.e. they are perpendicular to those (of the lamellar or lenticular domains) observed before the application of the field $E \parallel c$. This means that the field $E \parallel c$ can be treated as the origin of a new type of arrangement of regions polarized along the b -axis. This is an interesting experimental fact, because the c -direction is perpendicular to the b -direction. In figure 1, clear-cut domains with rectilinear walls are visible here and there, which is a rather unexpected result for TGS. Two photographs, taken for two different positions of the polarizer in relation to the analyser in the polarizing microscope, have been presented in order to show the existence of anti-parallel ferroelectric domains. It should be stressed that such stripe-like ordered regions are aligned along the c -axis independently of whether the transverse field is applied parallel or perpendicular to this axis [2]. As follows from our experiments, the original dielectric properties may be retrieved by annealing above T_c or by prolonged application of an alternating electric field of sufficiently high amplitude, parallel to the ferroelectric axis.

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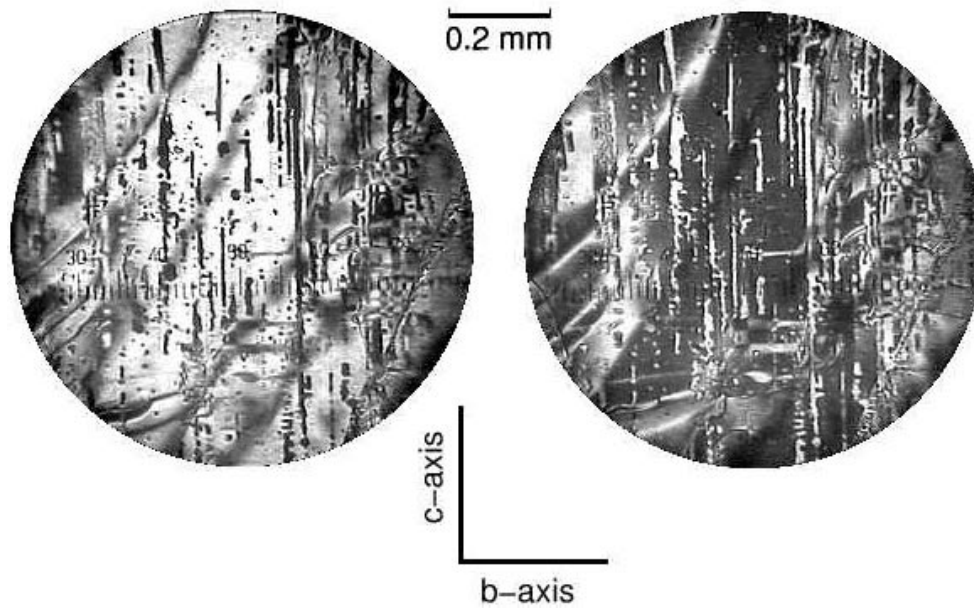


Figure 1. Domains, observed by means of the liquid-crystal technique, in the TGS sample previously exposed to a field $E \parallel c$ of 175 kV m^{-1} for about 50 hours; the same surface has been observed for two different polarizer positions in relation to the analyser in the polarizing microscope; the TGS sample used was not the same as that for which results are shown in the remaining figures.

On the other hand, it is a well-known experimental fact that the form of the electric susceptibility singularity of the original TGS sample at the critical point $T_c = 322.2 \text{ K}$ is somewhat different to that predicted by the Landau theory. The ratio $\chi(T_c + \Delta T)/\chi(T_c - \Delta T)$ measured experimentally for $0 < \Delta T \ll T_c$ usually differs from the value, equal to two, that follows from the mean-field approximation (the zero-field susceptibility critical amplitude quotient $\Gamma/\Gamma' = 2$ [3]). Moreover, measured electric permittivity values depend on the heating or cooling rate, experimental conditions, current domain configurations, history of the sample and amplitude and frequency of the measuring field [4–6]. It is also well known that the electric permittivity (susceptibility) of multi-domain crystals is higher than that of single-domain ones. As has been shown in [7], domain wall oscillations make a contribution to the permittivity values measured experimentally.

In the present paper we give the results of some investigations of dispersion phenomena for TGS samples previously exposed for a prolonged period to a transverse electric field. We point out that such a field may considerably and permanently change the temperature dependences of the permittivity for various frequencies of the measuring field.

2. Experiment

We present the results of electric permittivity measurements on a TGS crystal previously placed in a constant electric field $E = 175 \text{ kV m}^{-1}$ parallel to the c -axis in the Hoshino, Okaya and Pepinsky coordinate system [8] for about 329 hours (the influence of the field $E \parallel c$ can be easily observed even after just a few hours). Before that the crystal was annealed at 120°C for 20 hours without electrodes. In figure 2, the dimensions of the sample are shown

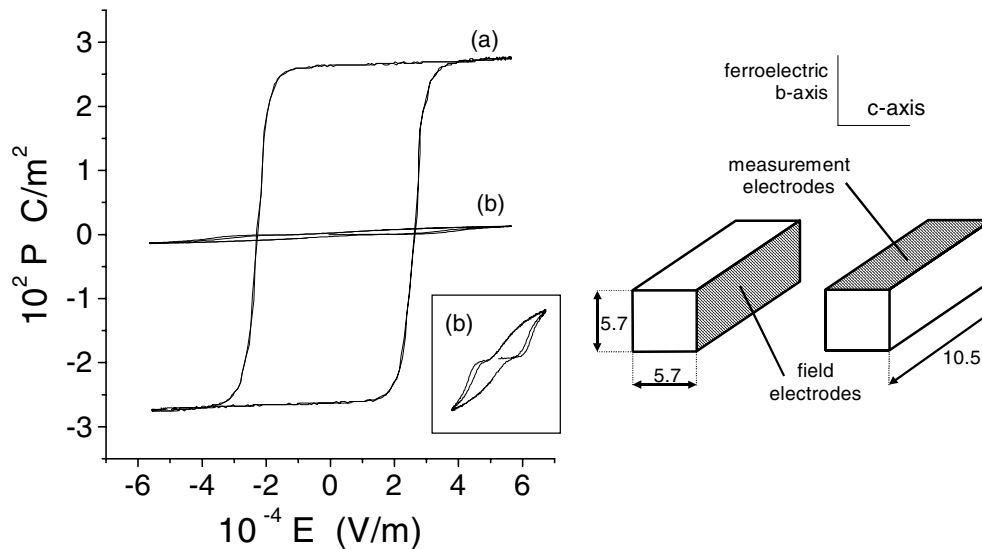


Figure 2. Dimensions (in millimetres) of the TGS sample together with the hysteresis loops: observed before (a) and after (b) the application of a field $E \parallel c$ of 175 kV m^{-1} for 329 hours at room temperature; inset: the loop (b) on a different scale (for two sine-wave cycles); for details, see the text.

together with the hysteresis loops observed before (a) and after the application of the field $E \parallel c$ ((b), inset). The silver-paste field electrodes (see figure 2) were replaced after the field $E \parallel c$ was switched off so that the hysteresis loop and permittivity could be measured along the b -axis by means of the measurement electrodes (figure 2). The Sawyer–Tower method with a driving-field frequency of 50 Hz was used for the hysteresis loop observation. The permittivity measurements were carried out at various measuring field frequencies of the LCR meter HP 4284A. The amplitude of the measuring field was 0.25 kV m^{-1} . The temperature was stabilized by means of an Oxford ITC 503 controller. In figure 2, the remanent polarization observed after the application of the field $E \parallel c$ (loop (b)) is about 100 times lower than that (loop (a)) of the original crystal, i.e. not influenced by this field. The narrowing in the middle, visible in the inset of figure 2, disappears in rather a short time (about a minute) after the Sawyer–Tower driving field has been switched on. However, a quasi-stable state of the TGS sample—with a single but considerably reduced hysteresis loop—may persist provided that this field is not applied for too long a time [1]. Our measurements were carried out about five months after exposure to the field $E \parallel c$ had been discontinued. There was no other prolonged exposure to fields during these five months.

3. Results

3.1. The transverse-field effect

A TGS sample with a reduced hysteresis loop, i.e. in the quasi-stable state described in the preceding section, was used for our permittivity measurements. In figure 3, the temperature dependences of the real part ϵ' of the a.c. permittivity are presented for various frequencies of the measuring field. The sample was heated at the rate 3 K h^{-1} . It became apparent that its behaviour is quite different to that of the original sample. Prior to the crossing of the critical

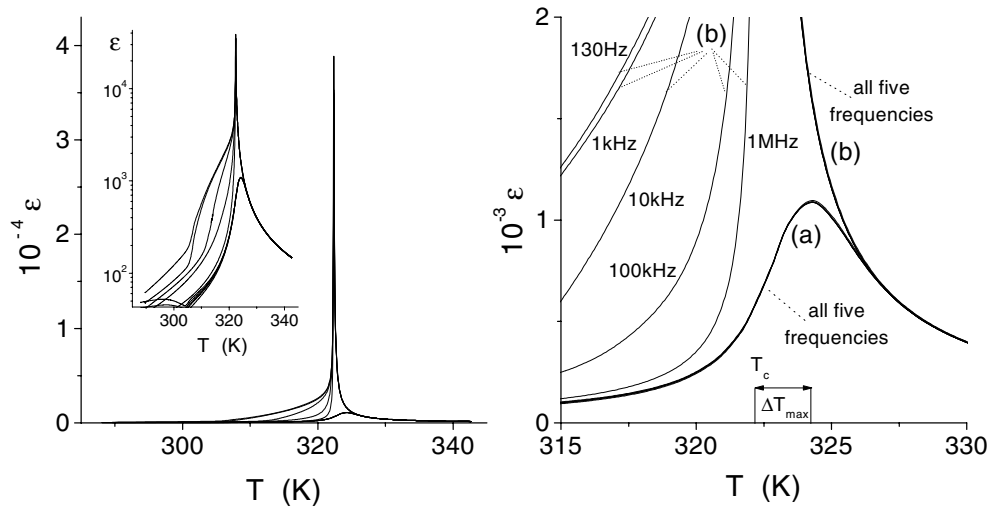


Figure 3. The temperature dependence (on various scales) of the real part ε of the electric permittivity obtained during heating after the application of a field $E \parallel c$ of 175 kV m^{-1} for 329 hours at room temperature (a) and after annealing at 100°C for 20 hours (b) for the following frequencies of the measuring field: 0.13, 1, 10, 100 and 1000 kHz; the dependences obtained before annealing coincide well for all five frequencies.

point, the sample still remained in the quasi-stable state with a considerably reduced hysteresis loop. As followed from our experiments, such a state could not be destroyed by the small LCR meter measuring field, of amplitude 0.25 kV m^{-1} . The ε -data coincided well for all frequencies and exhibited a single small maximum above T_c (figure 3, curves (a) and (b)). At first sight, such a shifted extremum appears qualitatively similar to that observed for TGS in the external electric field [9, 10]. However, the value of a parameter analogous to the quotient Q [10] is rather close to that measured for TGSe [11]. It should also be stressed that the sign of the shift $\Delta T_{max} \approx 2 \text{ K} > 0$ visible in figure 3 is at variance with the negative one observed after irradiation with monoenergetic electrons, with the beam directed parallel to the ferroelectric axis [12]. This suggests that the effects shown by us in the present paper cannot be caused by any damage due to electron penetration. The suppression of the dispersion phenomena observed in figure 3 is undoubtedly connected with anti-parallel c -domain freezing (figure 1) and with the remanent polarization reduction (figure 2), instead. Comparing the data in figures 1 and 3, we can conclude that there is considerable reduction of the domain wall oscillation contribution to the permittivity [7, 13] after prolonged application of a transverse field.

It should be added that similar effects have been observed by us after application of a field $E \parallel c$ for 70 hours at $T = 315 \text{ K}$. Thus the polarization reduction and the permittivity dispersion suppression have also been observed within the interval from room temperature up to T_c .

3.2. Domain instability at 304 K

It has been observed during heating of the crystal previously exposed to a field $E \parallel c$ at room temperature that, depending on the measuring-field frequency, local permittivity minima or inflection points occur at $T = T_s \approx 304 \text{ K}$, as presented in figure 4(a) for the same experimental data as in figure 3. Such an effect has been observed by us for a few TGS samples previously exposed to a field $E \parallel c$. Its intensity depends on the duration of the action of the field

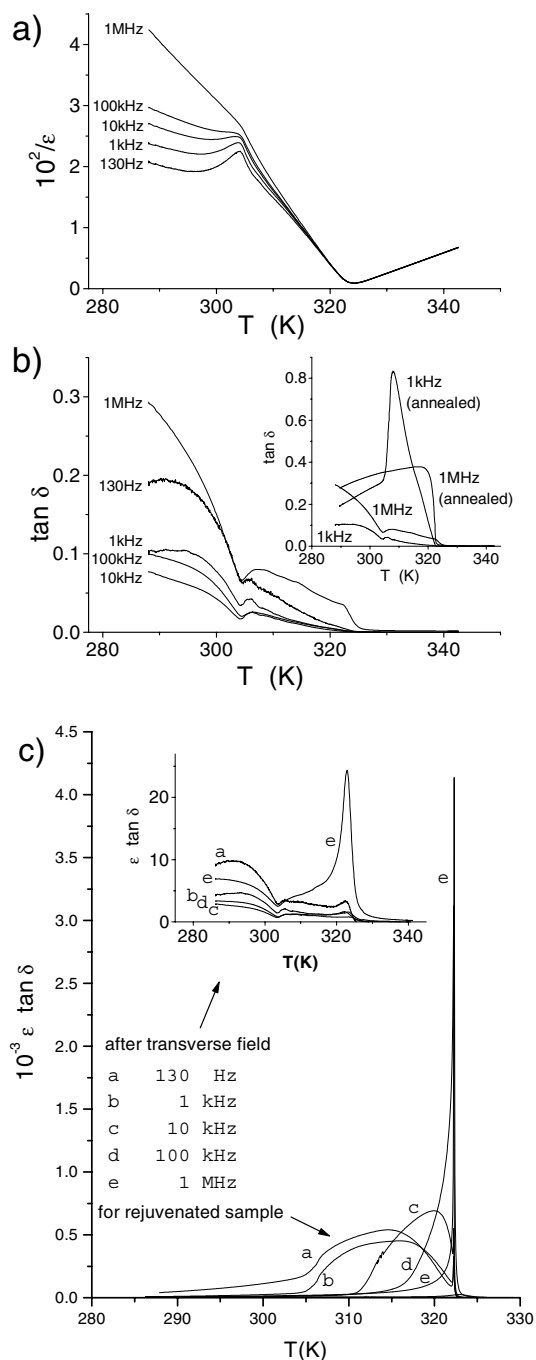


Figure 4. Temperature dependences of the inverse of the real part of the electric permittivity (a) and of the values of $\tan \delta$ (b) obtained during heating of the sample after the application of a field $E \parallel c$ of 175 kV m^{-1} for 329 hours at room temperature; the data for $\tan \delta$ and for the imaginary part, equal to $\epsilon \tan \delta$, of the permittivity obtained before and after annealing are compared in the inset of (b) for $f = 1 \text{ kHz}$ and 1 MHz and in the main diagram of (c); the values of $\epsilon \tan \delta$ obtained after the transverse-field treatment are so small that they are practically invisible in the main diagram of (c); an enlargement of them has been added in the inset of (c).

$E \parallel c$ as well as—we suppose—on the domain structure randomly formed just before this field treatment. For these reasons, the narrowing visible in figure 4(a) at $T \approx 304$ K may sometimes be observed only as a residual effect or even not be perceptible. It is an interesting experimental fact that, on the one hand, for the original crystal the dispersion enhancement is observed just above 304 K (see the inset of figure 3) while, on the other, its suppression takes place at the same temperatures as for the sample previously exposed to $E \parallel c$ (cf. figure 4(a) and the inset of figure 3). The conclusion is that some kind of domain structure instability may occur at $T \approx 304$ K. In the original TGS crystal, i.e. the one not exposed to the field $E \parallel c$, such an instability has been observed [14, 15] to lead to rearrangement of the domain structure. When the number of domains increases, the domain wall oscillation contribution to the permittivity seems to be dominant. A considerable enhancement of the permittivity values due to these oscillations is observed (cf. [7]). On the other hand, after the application of the field $E \parallel c$ at room temperature, the anti-parallel domain structure seems to become especially rigid just above 304 K. The almost complete disappearance of the contribution of the domain wall oscillation is then observed. Such freezing and also a relaxation process occurring above T_c make the permittivity maximum temperature higher than that for the original crystal.

The effect, visible in figure 4(a), is accompanied by the local minima of $\tan \delta$ at $T \approx T_s$ shown in figure 4(b). Consequently, the imaginary part of the permittivity (equal to $\varepsilon \tan \delta$) is completely suppressed (figure 4(c)). Its values are practically invisible (close to zero on this scale) in the main diagram of figure 4(c) because they are much smaller than those for the rejuvenated crystal. It should be stressed that the anomalies in the specific heat [16], in the domain density [14], in the domain wall surface energy [15] as well as in the temperature dependence of the electric resistivity (ρ) [17] have also been found at temperatures of 30–40 °C. Other types of change in the domain structure have also been observed [18–20].

3.3. The effect of rejuvenation

After the rejuvenation, the dispersion connected with the domain wall oscillation together with the original hysteresis loop (figure 2) can be observed again. The measurements of ε and $\tan \delta$ were repeated after annealing the sample at 100 K for 20 hours. The results obtained during heating are shown in figure 3. The original dispersion has been restored. The values of $\tan \delta$ are much higher than those observed before the rejuvenation (see the inset of figure 4(b)).

3.4. Comparison of the effects of transverse and longitudinal fields

As is known, the application of a longitudinal electric field $E \parallel b$, i.e. parallel to the ferroelectric axis, leads to the appearance of a single-domain structure in TGS. The question arises of whether such a structure is as stable as the anti-parallel one observed after the application of the field $E \parallel c$. In figure 5, the permittivity data obtained on the crystal previously rejuvenated by annealing and next placed in an electric field $E \parallel b$ have been shown. The field $E \parallel b$ of 123 kV m^{-1} was applied for 19 hours at room temperature; then it was switched off and the permittivity measurements were carried out while the crystal was heated. As the temperature increased, the homogeneous system of dipoles broke up into domains, so a distinct dispersion is clearly visible in figure 5. The corresponding results concerning the influence of a transverse field (from figure 3) as well as those observed for the young original sample, i.e. just after the rejuvenation by annealing above T_c (only for 1 kHz), have also been included in this figure, for comparison. At room temperature, just after both fields had ceased to be applied, the dispersion effects for $E \parallel c$ and $E \parallel b$ seemed to be comparable. However, closer to the Curie point, lack of dispersion was observed only for the crystal previously exposed to the transverse

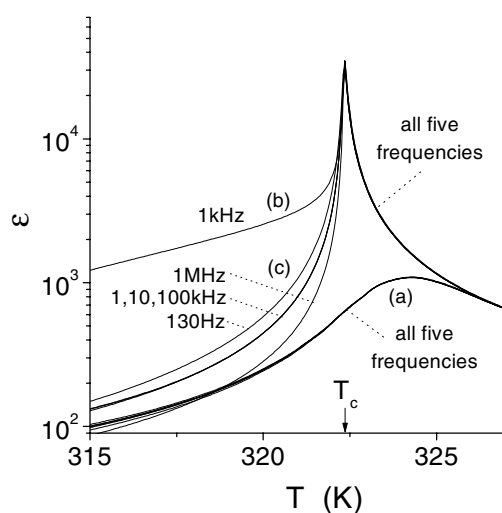


Figure 5. Temperature dependences of the real part ε of the electric permittivity obtained during heating of the sample after the application of a field $\mathbf{E} \parallel c$ of 175 kV m^{-1} for 329 hours (a), after the rejuvenation ((b); for clarity, only for $f = 1 \text{ kHz}$) and after the application of a field $\mathbf{E} \parallel b$ of 123 kV m^{-1} for 19 hours (c) on a semi-logarithmic scale; the frequencies of the measuring field were: 0.13, 1, 10, 100 and 1000 kHz.

field. It can also be noticed that after both the rejuvenation and the action of the field $\mathbf{E} \parallel b$, the permittivity maximum is observed at the same temperature, $T = T_c$, contrary to the result obtained for the crystal exposed to $\mathbf{E} \parallel c$.

After the prolonged application of a field $\mathbf{E} \parallel c$, the experimental values of ε for various frequencies of the measuring field seem to be very 'stable'. Each temporary permittivity increase induced by a high-amplitude alternating field applied for several seconds (e.g. the driving field $E \simeq 55 \text{ kV m}^{-1}$ in the Sawyer–Tower method) was followed by relaxation to the initial value. No permanent changes in the dispersion phenomena, caused conceivably by the destruction of the anti-parallel rigid domain structure due to the Sawyer–Tower driving-field action, have been observed in this case (cf. [1]).

4. Discussion

The appearance and freezing of anti-parallel c -domains due to the action of a field $\mathbf{E} \perp b$ seems to be the result of quite a different mechanism to that which is operative during the polarizing of the crystal in the field $\mathbf{E} \parallel b$. It is interesting that neither remanent polarization reduction nor c -domain formation was observed upon prolonged application of the electric field parallel to the ferroelectric b -axis. Some partial suppression of dielectric dispersion as a result of such field action is visible in figure 5, indeed. However, this effect is not so strong as that of the transverse field. In fact, the domain wall oscillation contribution to the permittivity has been found to be considerably and permanently reduced only after the application of a field $\mathbf{E} \parallel c$.

In general, we can state that prolonged exposure to a transverse electric field changes the direction of the anti-parallel domain wall normal from perpendicular to the c -axis [21] to parallel to it [2]. The question arises, however, of what the origin of such high stability of c -domains is. Below, we present a possible qualitative explanation of this experimental fact.

As follows from [22], the width W_0 of the stripe-like domain in the equilibrium state can be written as follows:

$$W_0 = [\gamma D P_0^{-2} (1 + \varepsilon_p^{1/2} \varepsilon_n^{1/2}) / 3.4]^{1/2} \quad (1)$$

where ε_p , ε_n are electric permittivities along the polar axis and the domain wall normal, respectively, D is the crystal thickness and γ is the surface energy of the domain boundaries. The above formula has been obtained as a result of minimization of the total free energy per unit area $F = F_{es} + F_w$, where F_{es} and F_w are the electrostatic and domain wall energies per unit area, respectively [22]. However, equation (1) only represents the state just after the formation of the stripe-like domain structure, e.g. after passage through the critical temperature on cooling. In fact, such a domain arrangement (and domain width) is expected to be changed with time due to the aging process. As follows from [22], the intensity of this process principally depends on the electric conductivity along the domain wall normal, σ_n . The larger the conductivity σ_n , the more rapid the domain structure changes. In the case of the original sample we have $\sigma_n = \sigma_c$, where σ_c is the conductivity along the c -axis. On the other hand, for the crystal previously exposed to a transverse electric field for a prolonged period, the conductivity σ_s measured along the direction perpendicular to both the b - and c -axes should be taken as σ_n . Because a strong anisotropy $\sigma_c \approx 100 \sigma_s$ was observed in [23], we can deduce that the domain structure that appears after the application of a transverse field should be much more stable than that of the original crystal.

So far, we do not know what molecular mechanism is responsible for the formation of c -domains in an electric field perpendicular to the ferroelectric axis. However, we are able to understand why they are so stable.

The original dielectric properties cannot be restored instantaneously. In figures 3 and 5 (curves (a)), a competition between two effects seems to be observed just after crossing the Curie point on heating. On the one hand, the rejuvenation process and therefore the permittivity enhancement start to be thermally activated and, on the other, the permittivity decrease with temperature takes place. Consequently, the suppressed permittivity maximum, shifted towards higher temperatures, is visible. It should be stressed that rather a low heating rate, equal to 3 K h^{-1} , was used during the measurements (figures 3–5). Nevertheless, in our opinion, the suppressed permittivity values obtained in the temperature interval $T_c < T \lesssim 326 \text{ K}$ do not seem to correspond to any absolutely stable states of the crystal. However, a very good coincidence of the results for various frequencies is worth stressing here. As mentioned above, the temperature dependence of the permittivity of the sample previously exposed to a transverse electric field for a prolonged period is only qualitatively similar to that of the original crystal when it is acted on by an electric field parallel to the ferroelectric axis. However, such a similarity leads us to suppose that the larger and larger paraelectric ‘islands’ appearing here and there in the crystal during the rejuvenation process are surrounded by regions that are still frozen. The reorientation of released dipoles may then be influenced by local internal electric fields. For this reason, no classical (e.g. Landau-like) phase transition is then observed.

The narrowing at 304 K, visible in figure 4(a) for the crystal previously exposed to a transverse electric field, can be considered to be related to the finding of an enhancement of permittivity at the same temperature but after the rejuvenation (inset of figure 3). The two effects seem to be connected with the same—but differently revealed—molecular mechanism. Although the narrowing observed at 304 K could not be directly caused by the transverse electric field applied at room temperature, some dielectric properties of the sample might have been permanently changed by electric charge flowing into the crystal then. Consequently, the considerable suppression of the dielectric dispersion took place at higher temperatures, i.e. above 304 K. Such an effect is undoubtedly connected to the disappearance of the remanent

polarization at a temperature much lower than T_c [2]. These results confirm our conviction that the permanent influence of the transverse electric field consists mainly in a space-charge distribution and therefore in a domain structure rearrangement. Under these circumstances, a quite new system of ordered regions may be favoured and stabilized due to enhancement of the electric space-charge density.

5. Conclusions

Summing up the results of the present paper, we can state that:

- (a) Suppression of dispersion phenomena is observed after prolonged application of an electric field perpendicular to the ferroelectric axis in the ordered phase. In particular, this is visible in the temperature interval $T_s \simeq 304 \text{ K} < T < T_c = 322.2 \text{ K}$; this is contrary to the results obtained for the rejuvenated TGS sample, where even an enhancement of the dispersion is observed for $T > T_s \simeq 304 \text{ K}$.
- (b) This means that the domain wall oscillation contribution to the permittivity is almost completely negligible after the application of the transverse electric field. However, the nature of the transition observed at 304 K in such more or less frozen systems of domains should still be investigated.
- (c) Alternating-current permittivity values much lower than those for the original sample are observed close to the critical temperature.
- (d) The temperature shift ΔT_{max} in the suppressed maximum of the electric permittivity is independent of the measuring-field frequency for $130 \text{ Hz} \leq f \leq 10^6 \text{ Hz}$.
- (e) The original dispersion properties can be restored by annealing in the paraelectric phase.
- (f) The anti-parallel multi-domain structure that appeared as a result of the action of the transverse field is much more rigid and more stable than that observed after the application of the field parallel to the ferroelectric axis.

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