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Metastable states in a triglycine selenate crystal plate

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Abstract

Measurements of the hysteresis loop and longitudinal electric susceptibility were carried out on a triglycine selenate [$(NH_2CH_2COOH)_3H_2SeO_4$] single crystal in the form of a round plate with an additional side electrode. The remanent polarization was initially reduced to zero due to a prolonged application of an electric voltage between the measurement and the side electrodes. Next, after voltage disconnection, a gradual transition from the crystal state characterized by the zero remanent polarization to the original state was investigated while alternately increasing and decreasing temperature. The remanent polarization started to noticeably increase each time the heating was interrupted and the crystal started to be cooled. The experimental data showed that the triglycine selenate (TGSe) crystal then behaved in such a way as if it 'remembered' the maximal temperature to which it had been heated after switching off the voltage. Such memory was also observed in the case of the longitudinal electric susceptibility measurements.
A freezing parameter was introduced in order to describe the experimental data.

1. Introduction

A few years ago it was found that the reaction of uniaxial ferroelectrics (triglycine sulfate, triglycine selenate, Rochelle salt) to an external electric field not parallel to the ferroelectric axis is quite different than that to a parallel one. The parallel field application leads to an instantaneous change in the position of the hysteresis loop or to a decrease or increase in electric susceptibility. All these changes are not permanent, though. After the parallel field has ceased to be applied, the uniaxial ferroelectric crystal tends more or less quickly to its zero-field equilibrium state.

The situation is quite different in the case of the field directed not parallel to the ferroelectric axis ([1–6] and references cited therein). Here the changes in dielectric properties caused by this field do not disappear after its disconnection [7]. There are many interesting experimental results obtained for such a field arrangement, although some of them have yet to be elucidated.

The transverse electric field, i.e. not parallel to the ferroelectric *b*-axis, can be applied to a single crystal in different manners, as shown in figures 1(a) and (b). In the case presented in figure 1(a), after disconnection of a prolonged transverse electric field (formerly applied due to the ΔV_A voltage application), a thin plate is cut out from the crystal so that electrodes perpendicular to the ferroelectric axis can be attached (after removal of the parallel ones). In the case in which the sample dimension along the *b*-axis is similar to that along which a constant field is applied, it is only electrodes that should be changed and no cutting is necessary. The influence of the formerly applied transverse electric field on the hysteresis loop or longitudinal electric susceptibility can be investigated by means of measurement electrodes perpendicular to the polar axis. Such investigations are feasible due to the permanent character of the changes induced by the transverse field. In fact, these changes seem to be caused by the appearance of metastable states. As follows from many experiments, a restoration of the original properties after the transverse field disconnection cannot take place instantaneously unless the crystal is heated above the critical temperature. In figure 1(b) a constant prolonged electric field is applied by means of two side electrodes (larger rectangles). The measuring field electrodes, in turn, are of the form of stripes perpendicular to the ferroelectric axis. Both fields can be applied simultaneously or one after another. One can see that in this case we deal with an inhomogeneous resultant electric field. However, many results obtained by means of such a two-pair electrode system have been at least qualitatively confirmed by measurements of crystals with electrodes, as in figure 1(a). This means that it is the electric field component perpendicular to the ferroelectric axis (or maybe also the lack of longitudinal polarization of the sample

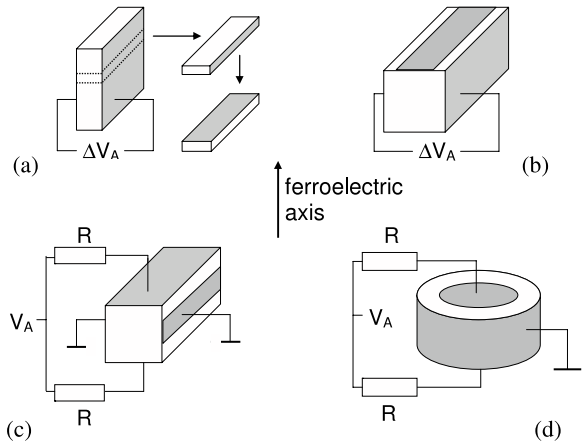

Figure 1. Different electrode-sample systems; ΔV_A—voltage, V_A—electric potential of both measurement electrodes; R—resistors (of the order of 10 MΩ each): a plate perpendicular to the polar axis is cut out after the transverse field disconnection and measurement electrodes are attached (a); four-electrode system (b); four-electrode system with the same constant potential on both measurement electrodes (c); three-electrode system with a grounded side electrode and the same constant potential on both measurement electrodes (d).

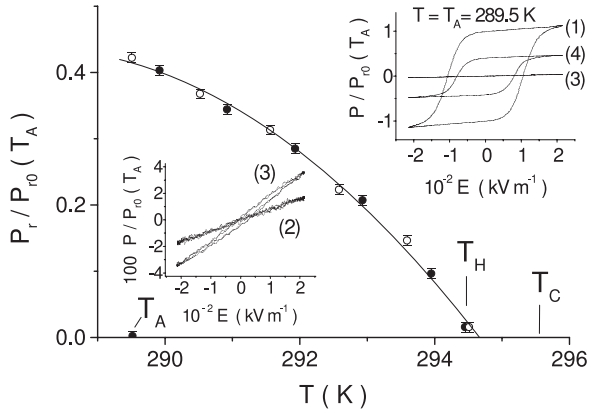

Figure 2. Reduced remanent polarization obtained in cooling (open circles) and heating (solid circles). The solid line is a second order polynomial fit. Bottom inset (both dependences for $T = T_A$): the lack of hysteresis loop just before the disconnection of E_I (2) and the result 28 h after this field is switched off (3); upper inset (all dependences for $T = T_A$): hysteresis loop of the original sample (1), 28 h after E_I disconnection (3) and after heating to T_H and cooling back to T_A (4).

as a whole) that plays a crucial role here. On the other hand, in many cases the system shown in figure 1(b) is more convenient. For example, to change electrodes means often to heat a crystal. As shown in [8], the triglycine sulfate (TGS) crystal of the form of perpendicular parallelepiped 'remembers' the temperature at which the transverse field was applied to it or the highest temperature to which it was heated after the transverse field disconnection. Such memory manifests itself by some changes in crystal properties observed when the sample is heated above these temperatures (partial rejuvenation).

In figures 1(c) and (d) the same constant electric potential is applied to both measurement electrodes, i.e. to larger rectangles or central circles in the cases (c) and (d), respectively. Additional blocking capacitors are then required in order to separate the measurement apparatus from a high potential [6, 9]. The side electrode potentials are equal to zero (grounded electrodes). However, an alternative arrangement is possible when a constant potential is applied only to the side electrodes (electrode). Then no blocking capacitors are required. There exists a constant electric voltage between the measurement and the side electrodes, as in the former case. It should be stressed that in the systems presented in figures 1(c) and (d)—due to their symmetry—the crystal is not polarized as a whole.

2. Experiment

Measurements of remanent polarization (of the hysteresis loop) as well as of the real part of longitudinal electric susceptibility $\chi = \chi_{22}$ and $\tan\delta = \varepsilon''/\varepsilon'$ were carried out on the triglycine selenate $[(NH_2CH_2COOH)_3H_2SeO_4]$ crystal, abbreviated as TGSe, with the electrode system shown in figure 1(d) (for $R = 12$ MΩ). The parameters ε' and ε'' are the real and imaginary parts of electric permittivity, respectively, and $\chi = \varepsilon' - 1$ (in the present paper the real part of susceptibility χ' is denoted by χ). The electric potential of the side electrode was equal to zero *ex definitione*. The diameter of the sample was 3.6 mm and its thickness was 1.4 mm. The diameter of the circular electrodes was 2 mm. All dimensions are given with an accuracy of 0.1 mm. The hysteresis loop measurements were done by means of the Sawyer–Tower method. The amplitude V_{D0} of the measuring alternating potential V_D applied to one of the measurement electrodes (cf [6, 9]) was 300 V. Its frequency was 100 Hz. The driving electric field E was assumed to be equal to V_D divided by the sample thickness (see inset of figure 2).

The hysteresis loop measurements were possible due to an application of the driving V_D potential. Results from earlier papers [7] concerning the transverse electric field application show that such an alternating potential causes a gradual rejuvenation (i.e. a restoration of the original properties) of the sample. However, in the case of the data shown in the present paper each single remanent polarization measurement lasted less than 1 min. The effect is therefore very much reduced here (although it may be sometimes visible, see below).

Electric susceptibility was measured on the same TGSe sample and with the same electrode system by means of the measuring field of frequency 1 kHz generated by an alternating V_M voltage of amplitude $V_{M0} = 0.3$ V. An HP 4284A LCR meter was used.

After annealing the sample (at temperature $T = 303.2$ K $> T_C = 295.6$ K, for a time not shorter than 10 h)—before each hysteresis loop or susceptibility and $\tan\delta$ measurement series—the prolonged constant electric potential $V_A = 500$ V and the alternating one V_D ($V_{D0} = 300$ V) were applied simultaneously to the measurement electrodes. Both potentials were a source of an inhomogeneous electric field E_I. Two blocking capacitors of 2 μF each were used in order to keep the Sawyer–Tower device (generating V_D) separate from the measurement electrode constant potential V_A, as in [6, 9].

3. Results

3.1. Hysteresis loop measurements

The annealed sample was exposed for 48 h to the inhomogeneous electric field E_I at $T_A = 289.5$ K. The field was generated simultaneously by two potentials: the alternating potential V_D and the constant potential $V_A = 500$ V. After switching off V_A and V_D—the temperature remained unchanged for $\Delta t = 28$ h. Next, the crystal was heated (for about half an hour) up to the temperature $T = T_H = 294.5$ K $< T_C = 295.6$ K at which it was kept for several hours. The measurements of the hysteresis loop in cooling started at $T = T_H$ almost two days (46.1 h) after the disconnection of the V_D and V_A potentials at $T = T_A$. One can see that the remanent polarization value at the starting point T_H was close to zero.

In figure 2 the open and solid circles concern the remanent polarization values obtained during a step-wise cooling and heating of the sample, respectively. At the temperature T_A one can observe then only a bit more than 40% of the remanent polarization value of the original (never exposed to any field) or rejuvenated (annealed above T_C) sample. What is interesting is that during the heating back up to T_H the same remanent polarization temperature dependence was measured as in the preceding cooling. This means that the crystal 'remembered' the temperature at which its remanent polarization had formerly risen. In general, different polarization dependences can be programmed by means of a transverse electric field and heat treatment (cf [10]). The remanent polarization will then tend to zero at different temperatures $T \leqslant T_C$. For example, quite a new $P_r(T)$ dependence (lying above that shown in figure 2) can be generated if the sample with completely reduced remanent polarization at $T = T_A$ is heated to the temperature $T = 295$ K. An additional conclusion is that hysteresis loops with the same non-zero remanent polarization $P_r < P_{r0}$ and different coercive field values can be observed at the same temperature, e.g. at $T = T_A$, for the same sample. One of such loops could be obtained as a result of isothermal freezing in E_I at T_A for not too long a time so that the polarization was only reduced to a non-zero $P_r < P_{r0}(T_A)$ value. Then no change in the coercive field takes place [6]. The second loop can be 'produced' in the way shown in figure 2 by choosing a proper value of the maximal temperature to which the sample is temporarily heated.

In the upper inset of figure 2 three hysteresis loops are shown, all of them measured at T_A: for the annealed sample as loop (1), 28 h after the disconnection of E_I (3) and after heating up to T_H and coming back down to T_A (4). One can see that not only the remanent polarization but also the coercive field is different in loops (1) and (4) measured at the same temperature. It is an interesting result because no changes in the coercive field have been observed in a transverse field at a constant temperature [6, 11]. The essential point here is that the change in the coercive field took place at T_A when the disconnection of E_I at this temperature was followed by a temporary heating of the sample.

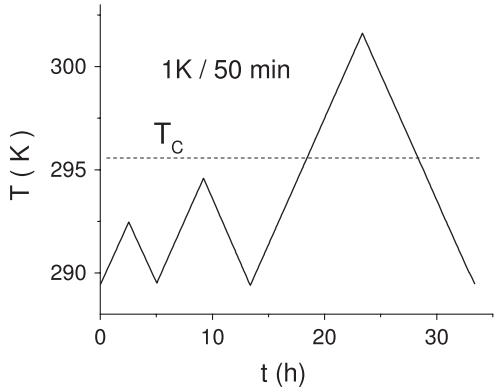

Figure 3. The way in which temperature was changed during the first stage of susceptibility measurements.

3.2. Susceptibility measurements

Measurements of the longitudinal electric susceptibility $\chi(=\chi_{22})$ were carried out in two stages. Before each of them the sample was annealed in the way mentioned in section 2. In both cases, just after annealing, the potentials $V_A = 500$ V and V_D (with $V_{D0} = 300$ V) were simultaneously applied for 48 h. After disconnecting the field E_I generated by these potentials, the measurement electrodes of the sample were connected to the LCR meter. Then susceptibility measurements were taken at different temperatures. The side electrode was grounded all the time. At the first stage the temperature was increased and decreased alternately at the rate of 1 K per 50 min, as shown in figure 3. It is interesting that the electric susceptibility does not stop increasing at the point where the change from heating into cooling of the sample occurs at T_1 or at T_2, as presented in figure 5. On the other hand, when the crystal is heated for the second and the third time one can see that just above T_1 and T_2, respectively, the susceptibility–temperature dependences return to their initial trend. In particular, such a kind of memory can be observed in figure 6, where the simultaneously measured values of tan δ have been shown. The parameter χ_A stands for the electric susceptibility measured at T_A just after the disconnection of E_I.

In figures 4–6 one can see also the results of measurements carried out in cooling from the paraelectric phase. The position of the susceptibility maximum observed then can be treated as the critical temperature T_C. Within the limits of experimental errors (± 0.1 K) this is in agreement with the results of the standard zero-field susceptibility measurements of the rejuvenated (annealed at $T > T_C$) sample.

During the second stage of the susceptibility investigations the sample—formerly annealed and then frozen in the field E_I in the same manner as at the first stage—was heated linearly at the rate of 1 K per 50 min from T_A up to above T_C. The data obtained in this way can be drawn as envelopes (dotted lines) of the dependences measured at the first stage, as shown in figures 4–6. The curves measured during the first stage of the susceptibility measurements start to coincide with such 'linear heating' envelopes just above the temperatures T_1 or T_2.

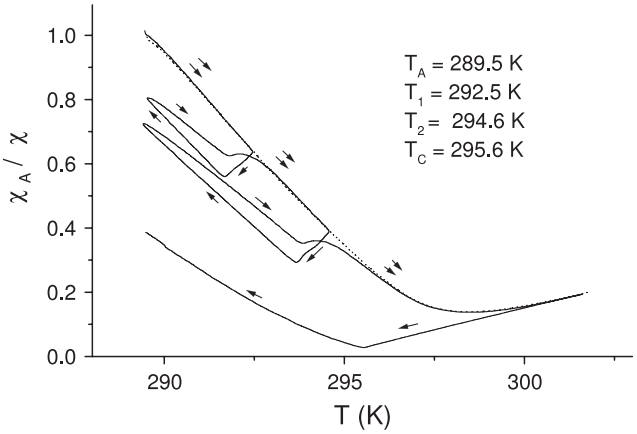

Figure 4. Inverse of electric susceptibility obtained after E_I disconnection as temperature was changing in the way shown in figure 3. The arrows indicate the temperature change; the dotted line envelope shows the second measurement when the temperature linearly increased; double arrows indicate that the dependences obtained in both measurements coincide; for χ_A, T_A, T_1 and T_2 see the text.

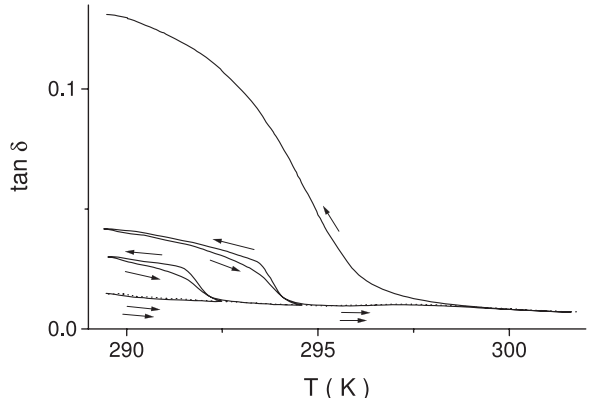

Figure 6. Values of tan δ obtained after E_I disconnection as temperature changed in the way shown in figure 3. The arrows indicate the temperature change; the dotted line envelope (hardly visible here due to the coincidence with the solid line) shows the second measurement when temperature linearly increased, double arrows at the very bottom indicate that the two dependences coincide; higher values are observed below T_1 and T_2 when the initial heating is interrupted.

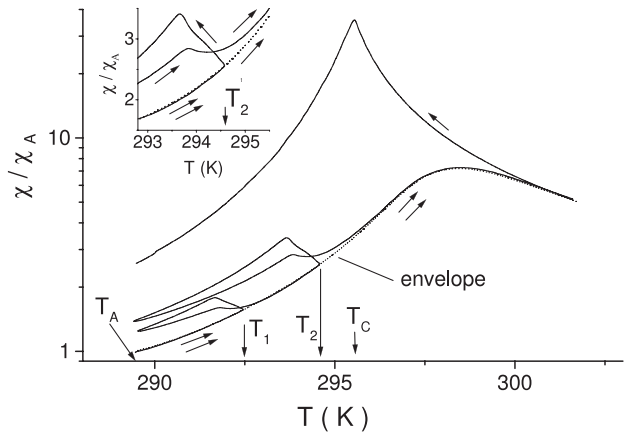

Figure 5. Electric susceptibility (semi-log scale) obtained after E_I disconnection as the temperature was changing in the way shown in figure 3. The arrows indicate the temperature change; the dotted line envelope shows the second measurement when the temperature linearly increased; double arrows indicate that the dependences obtained in both measurements coincide; the inset shows an enlargement.

4. Discussion

4.1. Freezing of dipole system

An application of a prolonged electric field not parallel to the ferroelectric axis leads to many changes in the dielectric properties of uniaxial ferroelectrics, including TGSe. The results of the present paper suggest that we deal with a similar situation also in the case of the electrode-sample system shown in figure 1(d). Some molecules of the crystal are supposed to be confined in metastable states also here, even after the disconnection of E_I. The sample then contains a lot of internal, not switchable, frozen domains (cf [11–13]). No spontaneous restoration of the original properties is possible when the sample is kept at a constant temperature in zero external electric field. In the bottom inset of figure 2 two results of the Sawyer–Tower type measurements are compared. The first, numbered by (2), was obtained just before the disconnection of E_I (see section 3.1). The second one, numbered by (3), was observed 28 h after switching it off. One can conclude that the rejuvenation noticed here after 28 h is very small in relation to the original loop (1), as shown in the upper inset of figure 2. What is more, there is every indication that such a spontaneous rejuvenation stops (or at most becomes much slower) several hours after the disconnection of E_I. Although small residual loops with P_r of about $10^{-2}P_{r0}$ can be visible then, they do not increase any more, at least within the next few days (no longer observations were done for the electrode system shown in figure 1(d)). The occurrence of such residual loops, visible in figure 2 (see also the lowest P_r values obtained at T_A and T_H), may be a consequence of the driving field application during former hysteresis loop measurements at T_A and T_H. A small accidental temporal heating above T_H (e.g. during the first stage of temperature stabilization) might have led to a partial rejuvenation of the sample, too. A reasonable explanation is also that, due to defects in real crystals, not all dipoles can be permanently frozen. It is just for this reason that a sample usually exhibits some residual hysteresis loop. The small non-zero value of P_r at T_H in figure 2 results probably from all the reasons mentioned above.

The hysteresis loop data shown in the main diagram in figure 2 were obtained within about 10 h (including both cooling and heating). The susceptibility measurements were carried out for about 20 h (figures 4–6) before the first transition to the paraelectric phase (when the rejuvenation started). These time periods mean that a very slow restoration process, even if it took place, did not influence the results of the present paper.

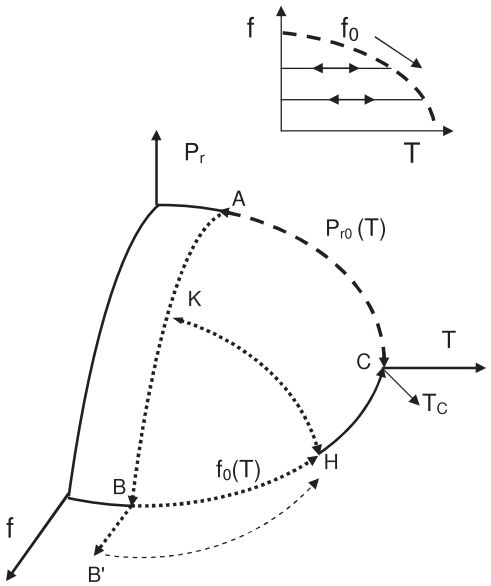

Figure 7. Schematic diagram in f–T–P_r coordinates. The path A–B–H–K–H corresponds approximately to the measurement results shown in figure 2, for details see the text. Inset: parameter f as a function of T, the dashed line concerns only heating after E_I disconnection, the solid lines are realized after each switching from heating along the dashed line to cooling.

4.2. Freezing parameter f

In order to describe the system after disconnection of the electric field E_I it is convenient to introduce a freezing parameter f. Figure 7 shows a schematic diagram in the f–T–P_r coordinates. The freezing parameter can have some physical meaning. For example, one can assume that $f \sim n$, where n is a concentration of free charge carriers which have been accumulated in the sample during the application of E_I. After disconnecting this field, some amount of such free electric charge can irretrievably flow out of the crystal. There is every indication that such an outflow stops when f has decreased to a temperature-dependent f_0 value. The parameter $f_0 \sim n_0$ corresponds to the minimal concentration n_0 required for the hysteresis loop to be completely suppressed ($P_r = 0$) at a given temperature. Even slight temperature decrease leads then to the instantaneous appearance of a non-zero P_r (cf [10]). This is because f_0 rises with decreasing temperature and at the same time the value of f remains unchanged.

As follows from the discussion above, there should exist a function $f_0(T)$ in which f decreases when the frozen crystal is quasi-statically warmed up to T_C. Obviously, this concerns only the first heating after the disconnection of E_I. Consequently, we deal then with a thermally activated outflow of free charges. However, this process is interrupted each time the sample stops being warmed, e.g. at T_H (see figure 2). Then the thermal activation of frozen dipoles ceases and we have $f = \mathrm{const}$ in cooling and heating for $T < T_\mathrm{H}$. This is shown schematically in the inset of figure 7. The dashed line $f_0(T)$ corresponds to the first heating after disconnection of the field E_I. The solid lines depict the states with $f = \mathrm{const}$. Every switching from heating (dashed line) to cooling (solid line) manifests itself by an instant appearance and increase in P_r (cf figure 2).

The solid line A–C in figure 7 depicts the temperature dependence of the rejuvenated sample (or the sample never influenced by any field). The dotted line A–B corresponds to an isothermal reduction of P_r due to an action of the electric field E_I. The fine dashed line (starting at B′) corresponds to the situation when the field E_I was applied for too long a time and the crystal started to be heated just after this field was disconnected. There is every indication that the distance between the B′–H and B–H paths depends on how long the sample was kept at T_A after switching off the voltages V_A and V_D.

The lines A–B–H–K–H correspond to the experiment shown in figure 2 if a small non-zero $P_r(T_\mathrm{H})$ value observed experimentally is neglected (see discussion in section 4.1). The H–K path represents the reversible heating and cooling between T_H and T_A. The parameter f remains then unchanged.

The discussion presented above explains the results concerning the remanent polarization data. A freezing of some groups of dipoles leads to a suppression of remanent polarization. Such rigid domains are stabilized by free charge carriers which can gradually flow out of the warmed sample due to the thermal activation of formerly frozen dipoles (a transition from metastable to stable states). In fact, such a process occurs in the case of the data shown in figure 2 but only when the sample is heated from T_A up to T_H for the first time after disconnection of E_I. Then we have $f(T) \approx f_0(T)$. When the reduced $P_r(T) \neq 0$ values are measured during subsequent temperature changes between T_A and T_H, the density of free charges is preserved (then $n \sim f < f_0 \sim n_0$ for $T_\mathrm{A} < T < T_\mathrm{H}$). Because f_0 increases with lowering temperature, fewer and fewer frozen dipoles can be stabilized while the sample temperature is moving down from T_H. This leads to the appearance and gradual increase in P_r (see figure 2). The $P_r(T)$ dependences are then repeatable (reversible cooling and heating) provided that the temperature of the P_r disappearance is not exceeded (in figure 2 this is somewhat above T_H due to the reasons mentioned above).

The interpretation of the susceptibility measurement results is similar, although there is some unexpected detail in the $\chi(T)$ dependence. One can see in figure 5 that the real part of susceptibility of the frozen sample does not stop to increase the moment the change from heating into cooling of the sample occurs. This looks as if the crystal were further heated for about an hour. The susceptibility starts to decrease only about one degree below the temperatures T_1 or T_2. It should be noticed that no analogous retardation exists at the maximal temperature in the paraelectric phase nor at T_A. In general, the less frozen the dipole system is, the higher are the susceptibility values measured. The freezing parameter f stops decreasing after switching from heating to cooling (cf inset of figure 7). Consequently, in figures 4–6, at a given temperature just below T_1 or T_2, we deal with two different dipole systems. The more rigid one (higher f) occurs before switching to cooling. The other one, somewhat softened, exists after the switching (lower f). Consequently, higher susceptibility values can be measured in the second case. However, about one degree below

T_1 or T_2, a natural tendency to decrease while moving away from T_C makes susceptibility values decline again.

5. Conclusions

Summing up the results of the present paper the following conclusions can be formulated:

(A) Some changes in dielectric properties—which have been formerly observed in a more or less homogeneous transverse electric field—are now presented for a TGSe round plate which is not permanently polarized as a whole.

(B) Quite new temperature dependences of remanent polarization and the real part of longitudinal electric susceptibility as well as $\tan\delta$ can be measured after disconnecting the inhomogeneous electric field E_I. Some kind of memory effect is additionally observed as the sample 'remembers' the maximal temperature to which it was heated after the last freezing process ceased.

(C) There exists the possibility of the occurrence of hysteresis loops with different values of remanent polarization and coercive field at the same temperature, for the same sample.

(D) There exists a parameter f (the freezing parameter) which exhibits a special temperature dependence $f_0(T)$ corresponding to the border line between $P_r = 0$ and $P_r \neq 0$. The parameter f can be considered proportional to the concentration of free charge carriers which stabilize the frozen dipole system.

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References

[1] Stoyanov S R, Michailov M P and Stankowska J 1984 *Acta Phys. Pol.* A **65** 141
[2] Ćwikiel K, Fugiel B and Mierzwa M 1999 *J. Phys.: Condens. Matter* **11** 7585
[3] Arunmozhi G, Gomes E de M and Ribeiro J L 2003 *Physica* B **325** 26
[4] Kalisz L, Fugiel B and Zioło J 1994 *Solid State Commun.* **89** 393
[5] Kikuta T, Nishizuka H, Yamazaki T and Nakatani N 2006 *Ferroelectrics* **336** 91
[6] Fugiel B 2008 *J. Phys.: Condens. Matter* **20** 255206
[7] Ćwikiel K, Fugiel B and Mierzwa M 2000 *J. Phys.: Condens. Matter* **12** 5033
[8] Fugiel B 2006 *Solid State Commun.* **137** 366
[9] Fugiel B 2008 *Eur. Phys. J.* B **61** 159
[10] Ćwikiel K, Fugiel B and Mierzwa M 2001 *Physica* B **296** 361
[11] Fugiel B, Ćwikiel K and Serweciński W 2002 *J. Phys.: Condens. Matter* **14** 11837
[12] Ćwikiel K, Fugiel B and Mierzwa M 2000 *Physica* B **293** 58
[13] Kikuta T, Yamazaki T and Nakatani N 2007 *J. Phys. Korean Soc.* **51** 754