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The influence of an electric field not parallel to the ferroelectric axis on the electric susceptibility of triglycine sulphate (TGS)

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Abstract. Susceptibility changes caused by an electric field applied in various directions not parallel to the ferroelectric axis have been measured both in paraelectric and in ferroelectric phases. An anisotropy of the relaxation phenomena has been found. Relaxation times of the order of 10^4 seconds have been observed.

1. Introduction

The anisotropy of the dielectric properties of triglycine sulphate (TGS) has been demonstrated in many papers. Data concerning piezoelectric, electrostrictive and elastic properties [1–8], the influence of a uniaxial pressure on the value of the Curie temperature [9] and the thermal expansion in various directions [10–16] are just some of the findings of such investigations.

The influence of an electric field not parallel to the ferroelectric axis on the electric permittivity, polarization, hysteresis loop and repolarization time was investigated in [17–19]. It was found that the largest changes in dielectric properties were for an electric field directed perpendicular to the main axis of a carbon–carbon bond in glycine I. However, as far as we are aware, the anisotropy of the time dependences of the electric susceptibility has not been investigated up to now.

2. Samples and experimental procedure

Below, we present the results of capacitance measurements on eight TGS samples cut out in various directions. Each was in the form of a perpendicular parallelepiped of dimensions $5.7 \text{ mm} \times 5.7 \text{ mm} \times 10.5 \text{ mm}$. Two pairs of silver paste electrodes were attached, as shown in figure 1. The measuring voltage U_m was applied to the narrower pair of electrodes. The normal, \vec{n}_m , to these electrodes was parallel to the ferroelectric axis. On the other hand, the vectors \vec{n}_i ($i = 1, 2, \dots, 8$) normal to the broader electrodes were directed as shown in figure 1. The high voltage U of the capacitor battery—acting as a source of electric field E not parallel to the ferroelectric axis—was applied to these electrodes. The measurement circuit is shown in figure 2. In the case of sample (1), the normal \vec{n}_1 was parallel to the a_{WH} -axis, where the subscript ‘WH’ refers to the coordinate system introduced by Wood and Holden [20]. For sample (2), \vec{n}_2 was perpendicular to the c_{WH} - and c_{HOP} -axes, where the subscript ‘HOP’ refers to the coordinate system proposed by Hoshino, Okaya and Pepinsky [21]. The normal \vec{n}_3 of sample (3) was parallel to the a_{HOP} -axis and that, \vec{n}_4 , of the fourth one was the normal

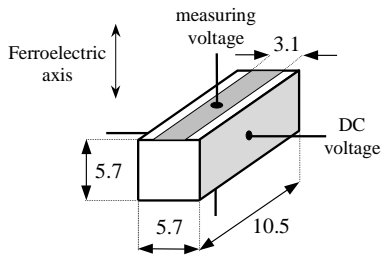
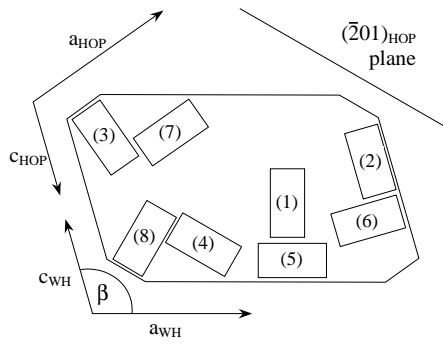


Figure 1. Eight samples, denoted by (1)–(8), cut out from a TGS crystal (the edge lengths of the crystal as a whole do not correspond to those grown) in various directions, and the electrode–sample system, with the dimensions (in mm) of the samples; in the top figure the ferroelectric axis b is perpendicular to the plane of the diagram; the normals \vec{n}_1 to \vec{n}_8 are perpendicular to the longer edges of the samples and to the b -axis.

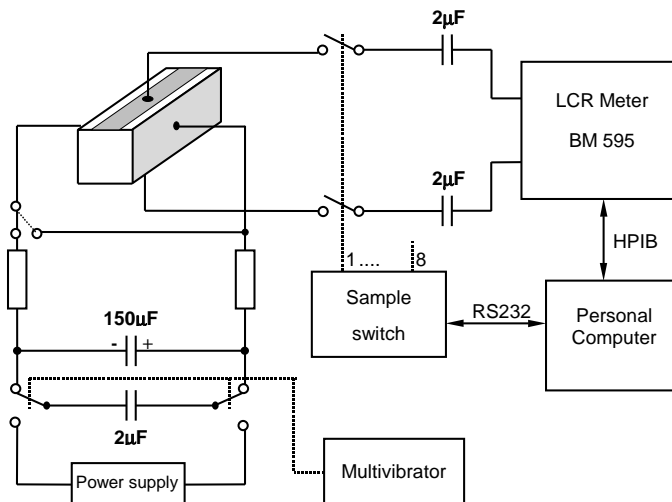


Figure 2. The measurement circuit with the capacitor battery represented by a resultant capacitance of $150 \mu\text{F}$.

to the $(\bar{2}01)_{HOP}$ plane. For samples (5), (6), (7) and (8) we have chosen $\vec{n}_5 \perp \vec{n}_1$, $\vec{n}_6 \perp \vec{n}_2$, $\vec{n}_7 \perp \vec{n}_3$ and $\vec{n}_8 \perp \vec{n}_4$, respectively.

The sample holder, with eight specimens, was locked in a copper block filled with silicon oil. In this way, almost simultaneous investigations of all of the samples, under the same thermodynamic conditions, were possible. The time of successive capacitance measurements of the eight capacitors together with the specimens (the mean value from ten measurements was

used for each crystal) was equal to about 20 s. The measuring voltage source (the LCR meter) was disconnected for 60 s after each registration cycle of eight capacitance values. In this way, every 80 s the measuring field was applied to a single specimen for about 2 s. The LCR meter TESLA 595 was used for the capacitance measurements. The amplitude and frequency of the measuring voltage were 1 V and 1 kHz, respectively. The capacitor battery, used as a source of voltage U , has been here represented by a resultant capacitance of 150 μF . The temperature was stabilized within an accuracy of 0.01 K. Two measurement series were carried out for the paraelectric phase. Before each of them, all samples were 'rejuvenated' by annealing at 358 K for about 48 h. Investigations of the ordered region were preceded by an annealing at 358 K for 16 h. The critical temperature T_c is equal to 322.25 K. The registration cycles and switching of individual specimens were controlled by computer. Because of the sample geometry (the inhomogeneity of E) we have not given values of the electric field strength E instead of the voltage U . For the same reason we could not calculate the susceptibility tensor. However, we were able to describe qualitatively the changes in the susceptibility χ or permittivity $\varepsilon = \chi + 1$ and also the anisotropy of the dielectric properties. Moreover, we show the geometry and dimensions of the sample–electrode system in figure 1. Such information may be helpful for approximately estimating both E and χ .

3. Results

3.1. Curie–Weiss law

In figure 3 the Curie–Weiss dependences of C_0^{-1} versus T are presented for all specimens, where C_0 is the capacitance of the capacitor together with a sample for an electric field $E = 0$. The temperature was lowered at the rate 0.002 K min^{-1} . For the paraelectric phase, the values of C_0 agreed well. This means that eight samples with very similar crystal–electrode-system geometry have been used. For the ordered region, the larger scatter of the data was

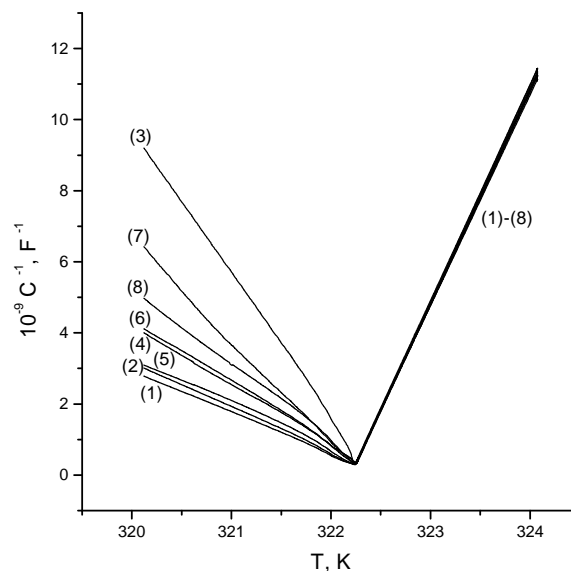


Figure 3. The dependences of C_0^{-1} versus temperature T obtained while cooling at the rate of 0.002 K min^{-1} for eight samples.

mainly due to outstanding individual domain structure. This effect should be rather treated as an experimental result dependent on the cooling rate. The susceptibility obtained in such a way below the critical point is not any stationary value. During the measurements on the ferroelectric phase described below, only stationary C_0 -values, i.e. capacitances of samples aged at $E = 0$ [22], were taken into account. These values are also treated as starting points in measurements of capacitance time dependences in non-zero electric field.

3.2. The influence of an electric field not parallel to the ferroelectric axis

The dependences of C versus time t for various temperatures have been measured under a constant voltage U switched on at $t = 0$. The results for samples (2) and (6) obtained above the critical temperature $T_C = 322.25$ K are shown in figure 4 for $U = 500$ V. The differences between the magnitudes and also the relaxation times are clearly visible for these two crystals. The ratios C_U/C_0 , i.e. the saturation values of $C(t)$ for $U = 500$ V divided by $C_0 = C(t = 0)$, are presented in figure 5 in a polar coordinate system (ϑ , C_U/C_0) for all samples at various temperatures. The eight ϑ -values correspond to the specimens denoted by (1)–(8). The smallest field effect was observed for sample (2). The rescaling of our data, as in figure 6, where dependences of $(C - C_U)/(C_0 - C_U)$ versus time have been drawn for all samples, leads to an interesting conclusion concerning differences between the relaxation processes for specimens (1)–(3) and (4)–(8). Such results suggest that a rather more complex molecular mechanism occurred in the crystals investigated. It is easy to see that for specimens (1)–(3) the relaxation rate depends on temperature. The lower the temperature is, the longer the relaxation process takes in the paraelectric phase (see the inset in figure 4). This means that some phenomena connected with a paraelectric–ferroelectric phase transition may be responsible for such behaviour (cf. [23]). For sample (2) the relation

$$f(t) = (C - C_U)/(C_0 - C_U) = e^{-t/\tau}$$

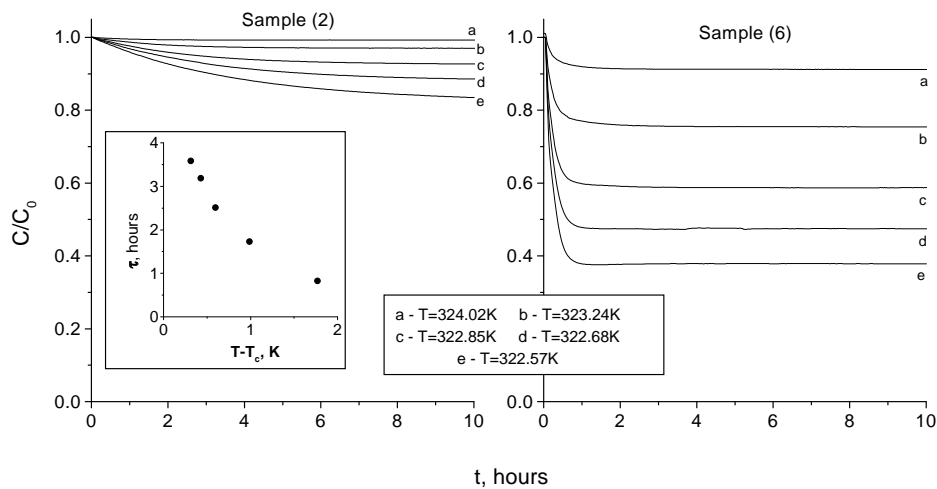


Figure 4. Examples of the dependences of C/C_0 versus time t for $U = 500$ V for samples (2) and (6) at various temperatures in the paraelectric phase; inset: the temperature dependence of the relaxation time for sample (2); the results shown in figures 4–6 concern the same measurement series; C_U -values for samples (1)–(3) have been determined for t much longer than 10 h.

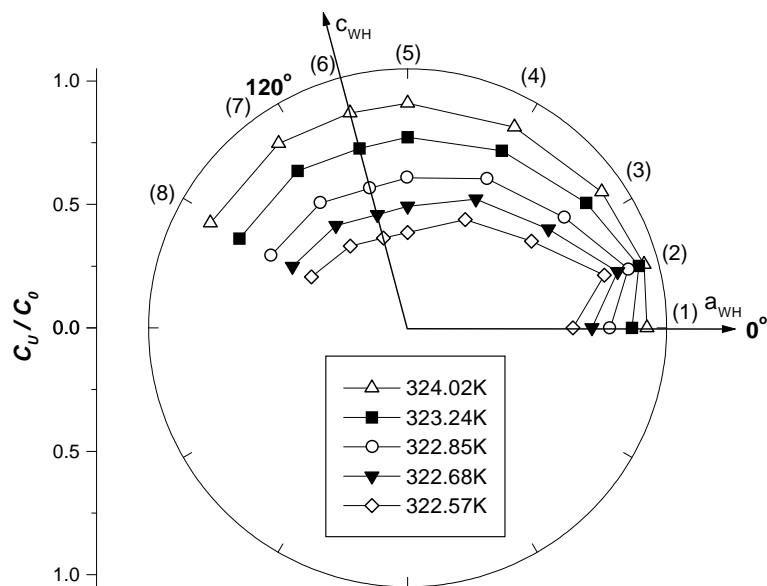


Figure 5. Examples of values of C_U/C_0 for eight samples, in the polar coordinate system, for $U = 500$ V and various temperatures in the paraelectric phase.

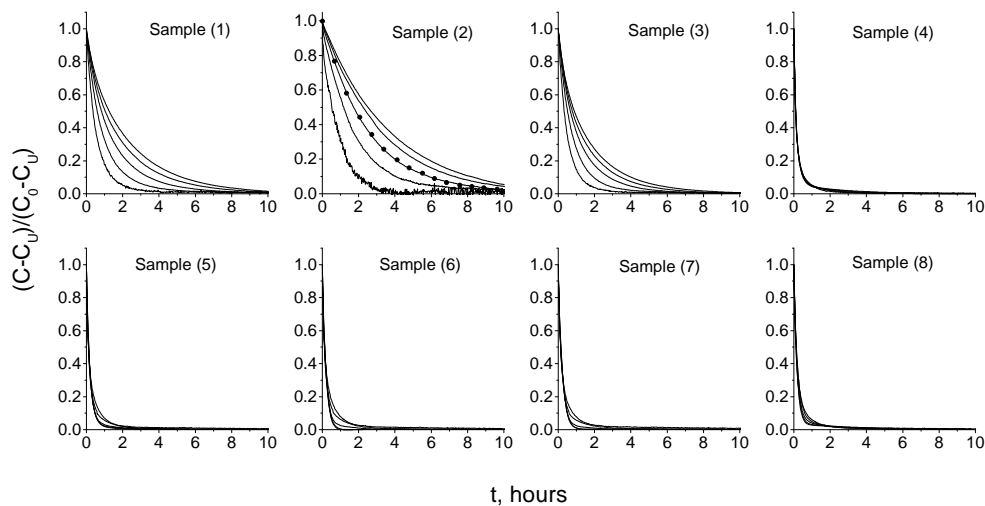


Figure 6. The time dependences of $(C - C_U)/(C_0 - C_U)$ for $U = 500$ V for eight samples at various temperatures: 322.57 K, 322.68 K, 322.85 K, 323.24 K and 324.02 K, in the paraelectric phase; the lower the temperature is, the longer the relaxation process takes for samples (1)–(3); a few points with coordinates $(t, e^{-t/\tau})$ for the fitted value $\tau = 2.54$ h have been added in the case of sample (2) for $T = 322.85$ K.

holds good, within the limits of experimental error, which is especially large for small $f(t)$. In figure 7, the experimental dependences of $\ln[f(t)]$ versus t are shown. A few theoretical points with coordinates $(t, e^{-t/\tau})$ for the relaxation time value fitted by the least-squares

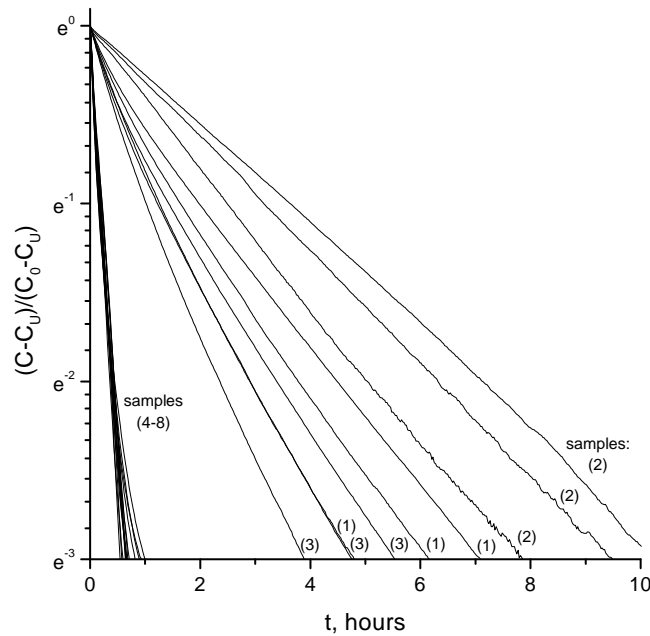


Figure 7. The time dependences of $(C - C_U)/(C_0 - C_U)$ for $U = 500$ V for eight samples at temperatures 322.57 K, 322.68 K and 322.85 K, on a semilogarithmic scale; the lower the temperature is, the longer the relaxation process takes for samples (1)–(3).

method, $\tau = 2.54$ h, have also been added for $T = 322.85$ K in figure 6 for sample 2. In the case of specimens (1) and (3), slight deviations from the exponential formula given above can be observed in figure 7. On the other hand, we have not found any monotonic temperature dependence for $C(t)$ functions for samples (4)–(8). As follows from figure 7, for sufficiently small time, the relaxation rate seems to be temperature independent in this case. However, deviations from the exponential formula given above should still be investigated in the future. The data shown in figures 6 and 7 enable us to divide the eight specimens investigated into two groups: samples (1)–(3) and samples (4)–(8). However, the relaxation time and the magnitude of $\Delta C = C_U - C_0$ are not the only parameters that are different for the two groups. For the ferroelectric phase, differences between the behaviours of samples (1)–(3) and samples (4)–(8) have also been found. In figure 8 examples of the dependences of C/C_0 versus time t are presented for all eight samples under $U = 500$ V at two temperatures, $T = 320.38$ K and $T = 321.65$ K. The dashed lines relate to the value of $C = C(t = 0) = C_0$ for $U = 0$. Just after the voltage increase from 0 V to 500 V, sharp maxima are visible. They are probably due to the domain reorientation process, because such a softening of the dipole structure usually enhances the electric susceptibility. The maxima are followed by susceptibility decreases similar to that observed for the paraelectric phase, and may be analogously interpreted. However, after the attainment of minima, the susceptibilities of samples (4)–(8) start to increase, as shown in figure 8(a). The highest positive susceptibility values are observed for sample (6). Closer to T_c , such an effect is clearly visible only for specimens (6) and (7) in figure 8(b). The relations between the magnitudes of the ‘negative’ and ‘positive’ effects vary with temperature, as is shown in figures 8(a), 8(b). We can state that two competitive mechanisms induced by an electric field E can be distinguished here. One of these, detected as a susceptibility decrease, seems to be similar to that observed in the paraelectric phase. The second one, visible as a

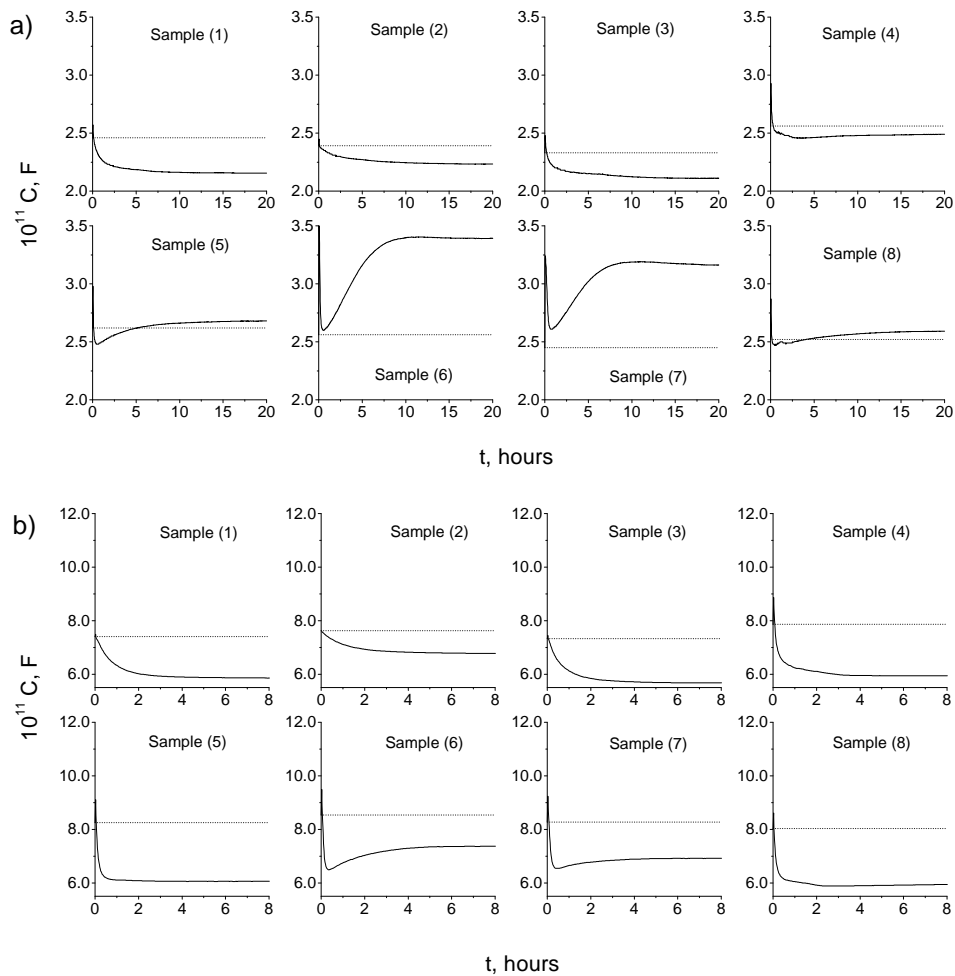


Figure 8. The dependences of C versus time t for $U = 500 \text{ V}$ for eight samples at two temperatures, $T = 320.38 \text{ K}$ (a) and $T = 321.65 \text{ K}$ (b), in the ferroelectric phase; dotted lines relate to values of $C = C(t = 0) = C_0$ measured just before switching on the voltage U (field E).

susceptibility increase, attains its highest value for sample (6). The residual contribution of a positive effect has also been found just above T_C . On the basis of the data shown in figure 8, we can state again that samples (1)–(3) differ from the others, because only for them has no minimum in the dependence $C(t)$ been observed.

It is an interesting experimental fact that the results for some specimens may be dependent on the history of the crystal and the experimental conditions. In figure 9(a) the ratios C_U/C_0 obtained during the other measurement series are shown. These investigations were carried out before those of figure 5. Between the two series of measurements, all samples were influenced by an electric field in both phases. As seen from figure 9(b), the earlier results are similar to those shown in figure 5 apart from the data for samples (5)–(7). In figure 9(b) the dependences from figures 5 and 9(a) obtained for almost the same temperatures are compared. It seems to be a rule that the closer to \vec{n}_2 the electric field direction is, the greater the reproducibility of the results observed.

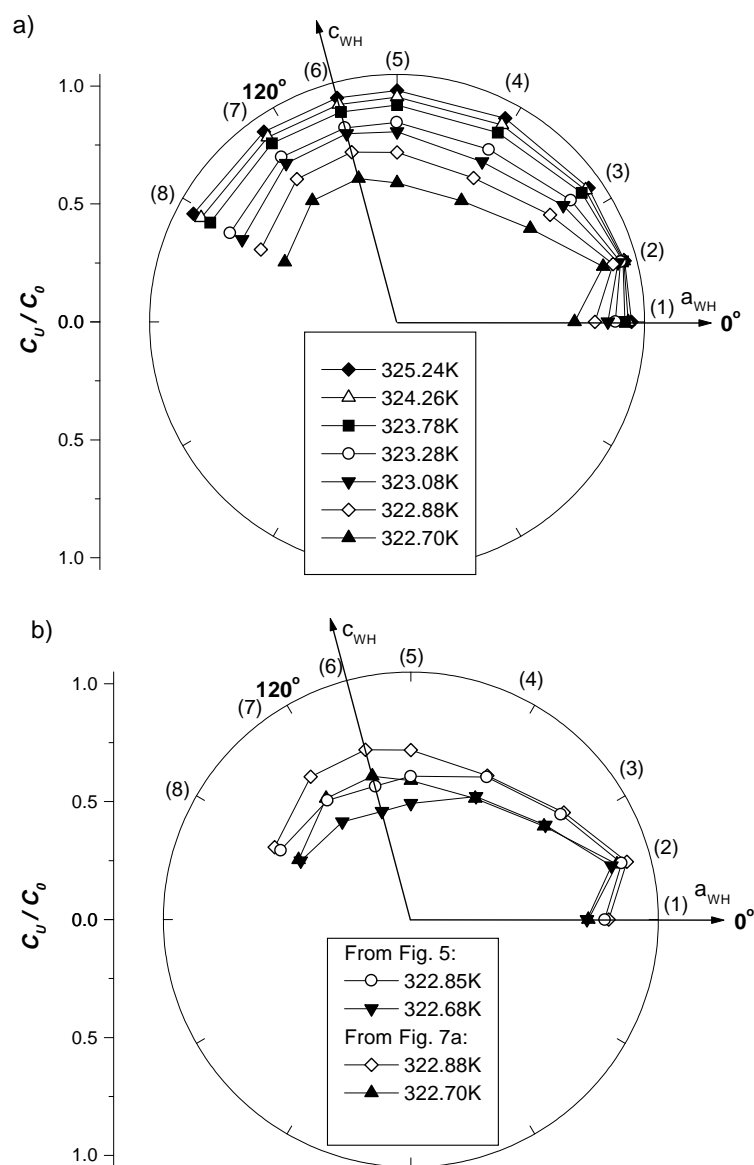


Figure 9. (a) Another example showing values of C_U/C_0 for eight samples, in a polar coordinate system, for $U = 500\text{ V}$, at various temperatures in the paraelectric phase (obtained earlier than those of figure 5); (b) comparison with the results for $T = 322.68\text{ K}$ and $T = 322.85\text{ K}$ from figure 5.

At the end of our investigations presented in this paper, the sense of the electric field E was changed at $T = 322.68\text{ K}$ just after the C_U/C_0 measurement series shown in figure 5 and also in figure 10 for positive U . The second half of the data in figure 10 were then measured for $U < 0$. Particular note may be taken of the C_U -values for samples (1)–(3), (7), (8). They seem to be independent of the field sense. Keeping in mind the data shown in figure 9(b), we suppose that the relations between the isotherms $C_U(U)$ for $U > 0$ and $U < 0$ may be

dependent on the history of the crystal. They remained unchanged, however, after the final return to the positive electric field E for $U = 750$ V at $T = 322.68$ K. The experimental points obtained in this way (not drawn in figure 10) coincide well with those in figure 10 for positive $U = 750$ V.

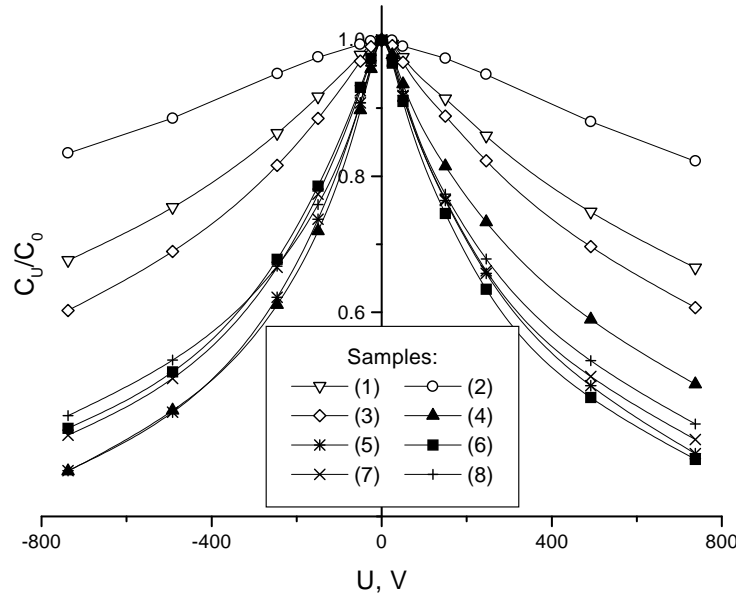


Figure 10. The dependences of C_U/C_0 versus U for eight samples at $T = 322.68$ K; a positive sign of E corresponds to the field configuration for all other figures; samples are denoted as follows: (1) downwards-pointing triangle, ∇ ; (2) circle, \circ ; (3) diamond, \diamond ; (4) upwards-pointing triangle, \blacktriangle ; (5) star, $*$; (6) square, \blacksquare ; (7) cross, \times ; (8) plus sign, $+$. Solid symbols (triangles and squares) relate to two samples with a 'reversal' effect; the voltage (electric field E) was changed from $U > 0$ to $U < 0$ after measurements of all C_U -values at positive U .

4. Discussion

Above T_c the capacitance C (electric susceptibility) changes due to application of a field E are negative, i.e. $\Delta C = C_U - C_0 < 0$ ($\Delta\chi < 0$) for all eight samples. The field sensitivity is the smallest for the field direction perpendicular to the c_{HOP} - (or c_{WH} -) axis. According to the papers [16, 21, 24, 25], the displacement of the NH_3^+ group of glycine I from the (010) plane gives the main contribution to the macroscopic polarization. The relatively weak bond between (glycine I) $^{1+}$ and SO_4^{2-} by way of NH_3^+ provides facilities for such a process. The electric field may hinder the libration of the glycine I molecule as a whole and the flipping motion of the NH_3^+ group (cf. [24]). Then a susceptibility decrease can be observed. Assuming such a model, we conclude that the smallest reduction of the freedom of motion of glycine I took place for sample (2) with \vec{n}_2 perpendicular to the c_{WH} - and c_{HOP} -axes. The question arises, however, of what the origin of such a c_{WH} - (and c_{HOP} -) axis distinction is in our experimental data. It should be stressed that the results of [6, 7] concerning piezoelectric and elastic properties also exhibit symmetry, approximately with respect to the c_{WH} - (and c_{HOP} -) direction. The significance of this direction has been confirmed in [26], where the results of impulse-stimulated light scattering measurements were given.

In the discussion above, however, no susceptibility time dependences have been taken into account. On the other hand, clearly visible anisotropy of a long relaxation process has been observed in our experiment. As was mentioned above, pre-transition phenomena seem to be responsible for the behaviour of the samples (1)–(3) because of the temperature dependences of the forms of their $f(t)$ functions (figures 6 and 7). On the other hand, an electric charge-transport contribution cannot be excluded, in particular in the case of samples (4)–(8). According to [27] (and references therein) the electric conductivity in TGS is the highest along the c_{WH} - (c_{HOP} -) axis. The differences between the results in figures 5 and 9(a) may just be due to the redistribution of charged particles in samples caused by electric fields of various directions. However, such an influence on the properties of crystals could not be controlled in our experiment. Consequently, therefore, we can only assume that the electric field treatment of all samples in both phases between the two measurements series—the earlier one presented in figure 9(a) and the later one presented in figure 5—might change some properties of the specimens. On the other hand, the question arises of whether any dielectric properties of TGS may be permanently modified by electric fields not parallel to the ferroelectric axis. In particular, up to now we have not been able to restore the results for samples (5)–(7), shown in figure 9(a), which were probably influenced by our initial investigations of these specimens. Neither change of the electric field sense as in figure 10 nor annealing at 358 K for about 48 h caused any reduction of the differences in figure 8(b).

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

- (a) A relatively long relaxation process has been observed in TGS in an electric field E not parallel to the ferroelectric axis. An exponential decay of the susceptibility over time has been found for sample (2).
- (b) In the paraelectric phase, the smallest susceptibility changes due to the application of the electric field E have been observed for sample (2) with \vec{n}_2 perpendicular to the c_{WH} - (c_{HOP} -) direction. The longest relaxation process was also found for this specimen.
- (c) Three effects induced by an electric field have been distinguished. One of these has been detected in both phases as a susceptibility decrease. Two remaining ones, sharp maxima and, especially large for samples (5) and (6), highly anisotropic positive field effects, have been observed only in the ferroelectric phase, although the possibility of existence of the latter above T_c as a residual contribution cannot be excluded.
- (d) The reproducibility of the experimental results depends on the electric field configuration.

Unfortunately, apart from the discussion above, we cannot interpret our data in detail purely on the basis of dielectric investigations. It may be possible to explain the susceptibility changes following spectroscopic measurements of the crystal molecular structure as well as additional conductivity investigations in electric fields of various directions.

Acknowledgments

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