DOMAINS AND IMPERFECTIONS IN FERROELECTRIC TGS

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ABSTRACT — Dielectric constant, polarization and pyroelectric coefficient of ferroelectric TGS are investigated near the phase transition. The values of the critical exponents β, δ, γ and γ' are in agreement with those predicted by a mean field theory. The dielectric constant values are strongly influenced by domain formation. Domain relaxation seems to obey a «stretched» exponential law.

1 – INTRODUCTION

Triglycine Sulfate (TGS) – $(NH_2\,CH_2\,COOH)_3 \cdot H_2SO_4$ – is a uniaxial, order-disorder ferroelectric with a second order phase transition at ~322K [1]. Deuteration has a small effect on its ferroelectric properties.

TGS crystallizes with the symmetry of the monoclinic system. In the high temperature phase its symmetry group is C_{2h} with the binary axis parallel to the b axis of the monoclinic system. In the ferroelectric phase the symmetry group is C_2 and the polarization in TGS is associated with the glycine molecules [2].

Although intense study has been made on triglycine sulfate's dielectric behaviour and a good agreement with the Mean Field Theory is usually obtained, there are still a few aspects that need to be clarified. In fact the ratio of the slopes of the reciprocal dielectric constant (ε^{-1}) versus the temperature below and

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above T_c (m_1 / m_2) yields values higher than the value 2 predicted by Landau's theory of phase transitions [3, 4, 5, 6]. The adiabatic correction suggested by Triebwasser [7] is not enough to obain a value of 2. The factors that are usually presented as being responsible for such a behaviour are: the existence, in the sample, of superficial layers with a small dielectric constant [8, 9, 10] and, in polydomain samples, the electrostriction effect caused by the formation of differently oriented domains. In addition, the study done by Gonzalo [11] and Sekido & Mitsui [10] suggests an infinite value for the dielectric constant at the transition, while other authors [12] find that it has a finite value.

Our purpose is to try to clarify this situation, as well as to verify the importance of surface treatments. Fatigue caused by the application of electric fields, and the influence of domains in TGS are also studied. We measured the dielectric constant, pyroelectric coefficient and spontaneous polarization as functions of temperature in differently prepared samples and we analysed the results obtained.

2 – EXPERIMENTAL PROCEDURE

The samples (1, 2 and 3) used in our study had the shape of thin slices, of different surface shapes, perpendicular to the b axis,

TABLE I — Dimensions and preparation of the measured samples

Samples		1	2	3
Extraction from mother crystal		cleavage	cleavage	cut
Surface polishment		water	water	diamond paste (1 μ)
Dimensions	Area (mm^2)	37.1	13.5	32.0
	Thickness (mm)	1.2	1.0	1.6
Max. temperature (°C) subjected during preparation		70-80	70	room temp.

and were obtained from different parts of the same TGS single crystal. Their characterization is summarized in Table I.

All samples had excellent transparency and no tensions or defects could be detected when analysed in a polarization microscope. We used silver paste as electrodes, and during measurements all samples were free from any clamping.

To measure the complex dielectric constant, we used a five terminal coaxial method [13] with a resolution of about 0.01 pF.

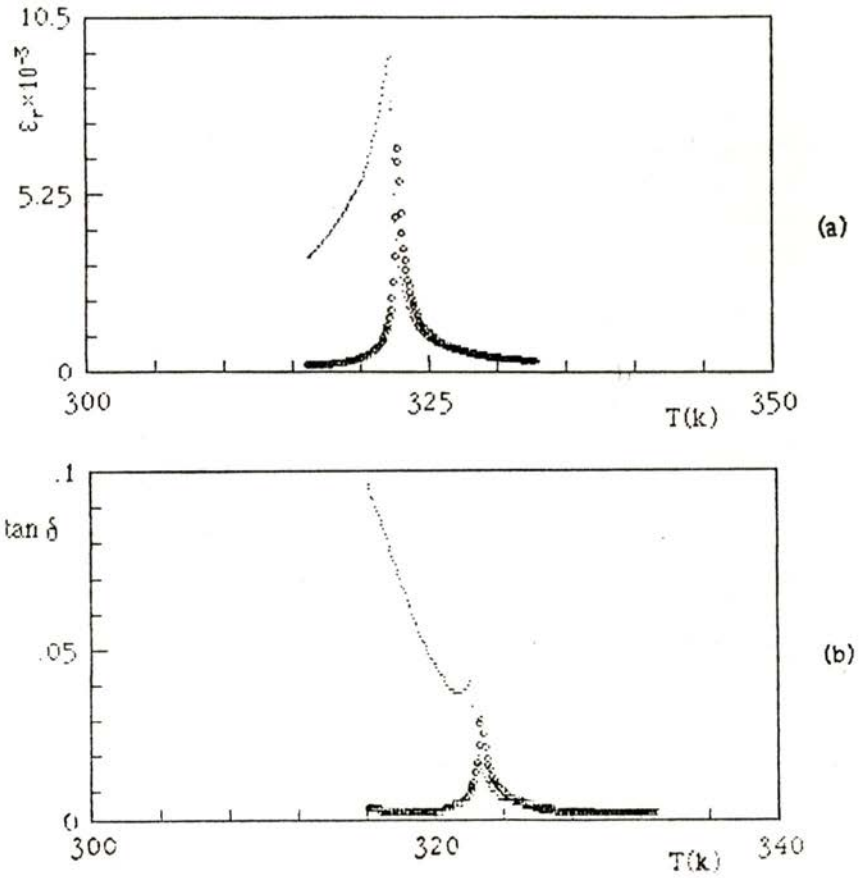

Fig. 1 — Relative dielectric constant (a) and loss, tan δ (b) as function of temperature, in sample 3, during: o → heating; • → subsequent cooling down. These measurements were taken at 1 kHz.

The data acquisition was done automatically through an IEEE bus. We chose a 1V amplitude measuring signal with frequencies of 1 kHz or 10 kHz.

A copper-constantan thermocouple was used to measure the sample's temperature and we had a temperature stability of about 0.02K.

The pyroelectric coefficient was measured by studying the pyroelectric current under short-circuit conditions [14] using an electrometer with a resolution of about 1×10^{-14}A. The data acquisition was done automatically through a BCD bus. To achieve a monodomain the samples were always cooled from the paraelectric phase under an electric field of about 0.8 kV.cm^{-1}. When the intended temperature was attained, the field was removed and the samples' electrodes shortcircuited during a few hours, eliminating in this way any residual spatial charges. Measurements of the pyroelectric current were then taken, when warming up the sample at a heating rate of about 0.1K per minute at the transition.

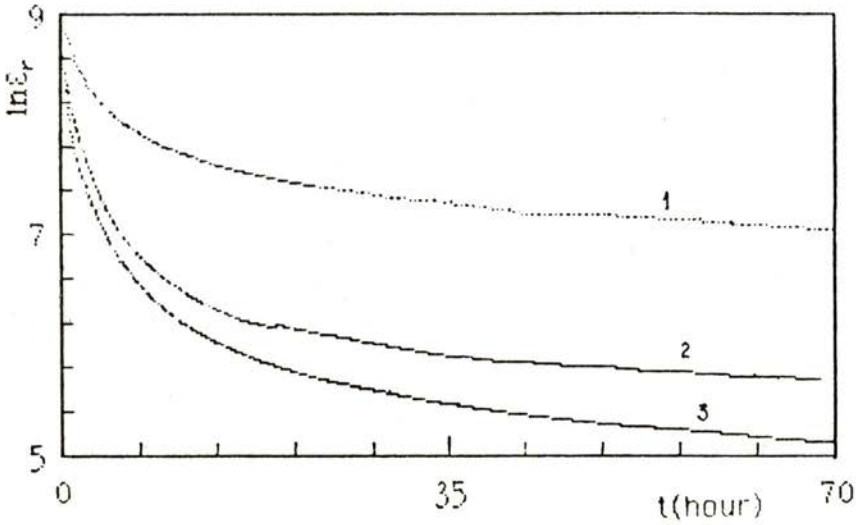

Fig. 2 — ln ε_r vs. time in the ferroelectric phase at constant temperatures $T_1 < T_2 < T_3$. These measurements were taken after cooling the sample through the phase transition.

To study the polarization reversal we used a modified Sawyer-Tower circuit [13]. The alternating electric tension applied to the samples had a frequency of 0.2 Hz and an amplitude of about 500 V.

3 — RESULTS AND DISCUSSION

The results obtained by us clearly show that the values of the relative dielectric constant ε_r and loss $\tan\delta$ are systematically smaller on heating the samples through the phase transition than on the subsequent cooling down. An example of this behaviour is shown in Fig. 1 and it is associated with the fact that the domain structure of TGS ferroelectric phase takes some days to relax to equilibrium. Until it does, the response (ε_r) to the measuring field has a higher value than the equilibrium one, due mostly to domain wall motion. This behaviour is shown in the time dependence of $\ln \varepsilon_r$ depicted in Fig. 2, for a sample other than the three already referred. In this figure we can see that the relaxation behaviour is not an exponential one. We found that

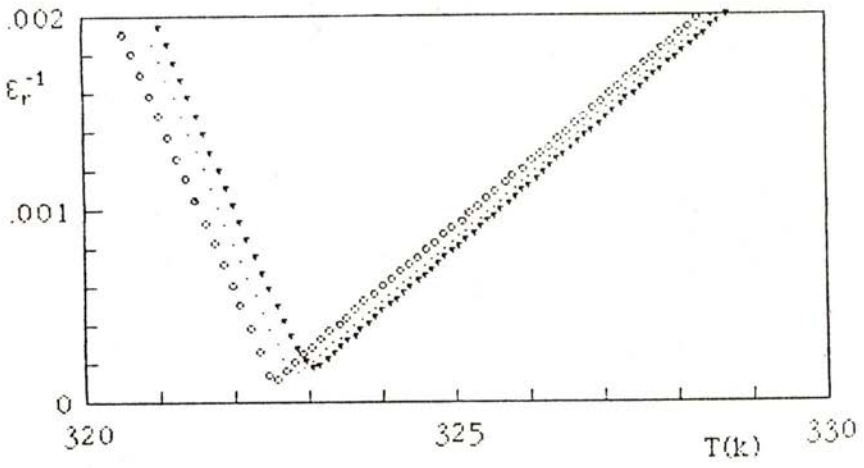

Fig. 3 — Inverse of relative dielectric constant ε_r^{-1} vs. temperature T, for three consecutive heatings relating to sample 3: o → heating on virgin sample; • → first heating on monodomain sample; ▾ → third heating on monodomain sample.

TABLE II — Values of ε_r max., temperature at ε_r max. and ratios m_1 / m_2 calculated in the ranges of 2K or 5K around T_0, for the three samples studied. The electric field used on the samples to achieve a monodomain was 0.8 kV cm^{-1} except on the first heating of monodomain sample 1. In this case the electric field was ~0.4 kV cm^{-1}

Number of sample	Consecutive warm ups of the sample	ε_r max.	Temperature T_0 at ε_r max. (K)	m_1 / m_2 in the range of	
				2K around T_0	5K around T_0
1	1st heating on monodomain sample	10285.71	323.06		2.6
	2nd heating on monodomain sample	9218.33	322.94		2.83
2	heating on virgin sample	59925.93	322.59	3.42	3.23
	1st heating on monodomain sample	39185.19	322.66	3.62	3.30
3	heating on virgin sample	8998.87	322.59	2.76	2.82
	1st heating on monodomain sample	6612.65	322.86	2.72	2.90
	3rd heating on monodomain sample	6046.38	323.05	2.83	3.03

the data concerning ε_r versus time could be satisfactorily fitted to the expression [15]:

$$\varepsilon_r = \varepsilon_0 \exp [- (Ct)^m]$$

where $\varepsilon_0 = \varepsilon_r$ for $t = 0$ and C and m are parameters.

Because of this, only measurements when heating a sample with its domain structure in equilibrium – virgin or monodomain sample – were analysed. To achieve a monodomain, we followed

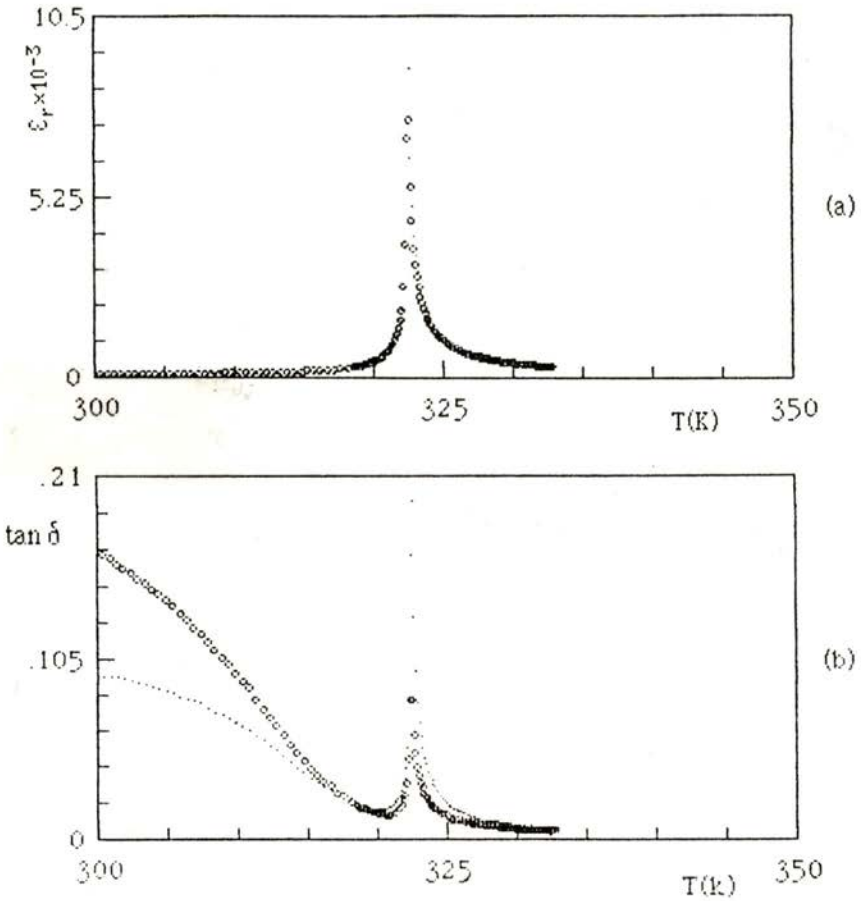

Fig. 4 — Relative dielectric constant ε_r vs. temperature T (a) and loss tangent tan δ, vs. T (b) relating to virgin sample 3. These measurements were taken when heating the sample at the frequency of: • → 1 kHz; o → 10 kHz.

the same procedure as in the pyroelectric measurements. Although the electric field used to achieve a monodomain was not high, it still caused some 'fatigue' in the material, as can be seen from results concerning sample 3 (Table II and Fig. 3). One should also note in Fig. 3 that ε_r has finite values at the phase transition, in agreement with the results obtained by Graig [13].

The influence of the sample surface treatment on the behaviour of ε_r vs. temperature can be observed in the maximum values of ε_r for the three samples, and is presented in Table II. In this table we can also see that the values for the ratios m_1 / m_2 in monodomain sample 3 (no clamping by domains) are definitely higher than Landau's value. The adiabatic factor correction can be responsible, at the most, for a reduction of 20 % [7]. But even with this correction the value obtained is higher than 2.

Hill & Itchiki [16] found that in the ferroelectric phase, when the frequency of the measuring signal is increased, the loss tangent has lower values than at lower frequencies. We have found the inverse, as can be seen in the example presented in Fig. 4. It is also displayed in this figure the temperature dependence of the dielectric constant, which is quite similar at the frequencies of 1 kHz and 10 kHz.

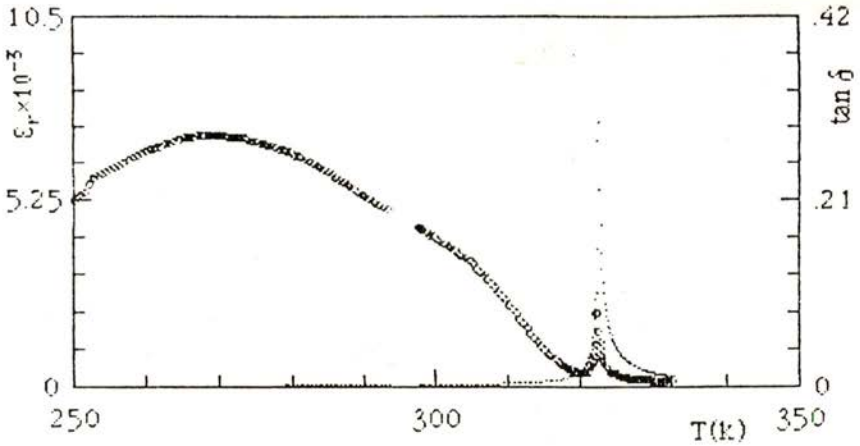

Fig. 5 — Measurements of ε_r vs. T (•) and tan δ vs. T (o) relating to sample 3. The virgin sample was cooled from room temperature to ~250K and then heated at the frequency of ~10 kHz. The data acquisition was momentarily interrupted at around ~295K.

Itoh & Mitsui [17] observed round peaks in the temperature dependence of the dielectric constant at low temperatures. Our results (Fig. 5) show that only the loss tangent has a round peak at low temperatures.

From the pyroelectric current I measured as a function of the temperature in samples 1 and 3, we obtained the pyroelectric coefficient and the spontaneous polarization P_s shown in Fig. 6.

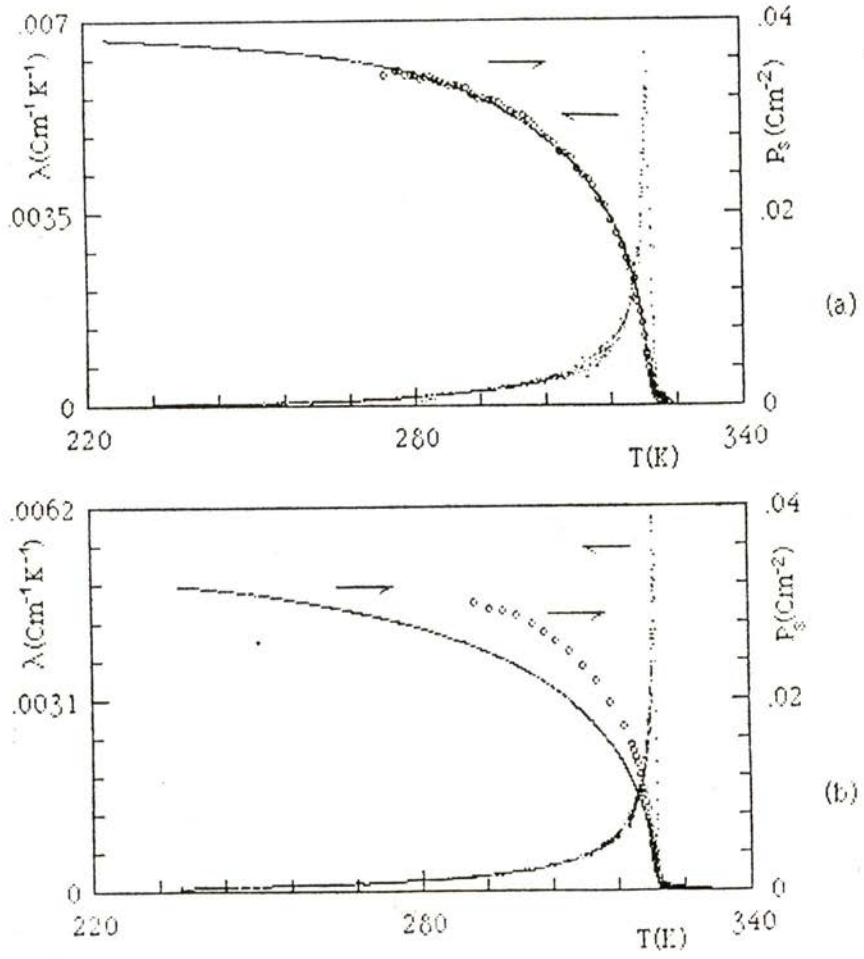

Fig. 6 — Spontaneous polarization P_s and pyroelectric coefficient λ vs. temperature T on sample 1 (a) and on sample 3 (b). • → λ vs. T; o → P_s vs. T, obtained from hysteresis loops; - → P_s vs. T, obtained from integration of λ.

Using the procedure previously described we obtained hysteresis loops in samples 1 and 3, examples of which are depicted in Fig. 7.

The 'squareness' of the hysteresis loops obtained for samples 1 and 3 proves the good quality of the samples. The fact that we always obtained a good saturation of the hysteresis loops for any of the samples shows that a monodomain is actually achieved when following the procedure referred in the previous pages. It is worth noting (Fig. 7) that while the lower coercive

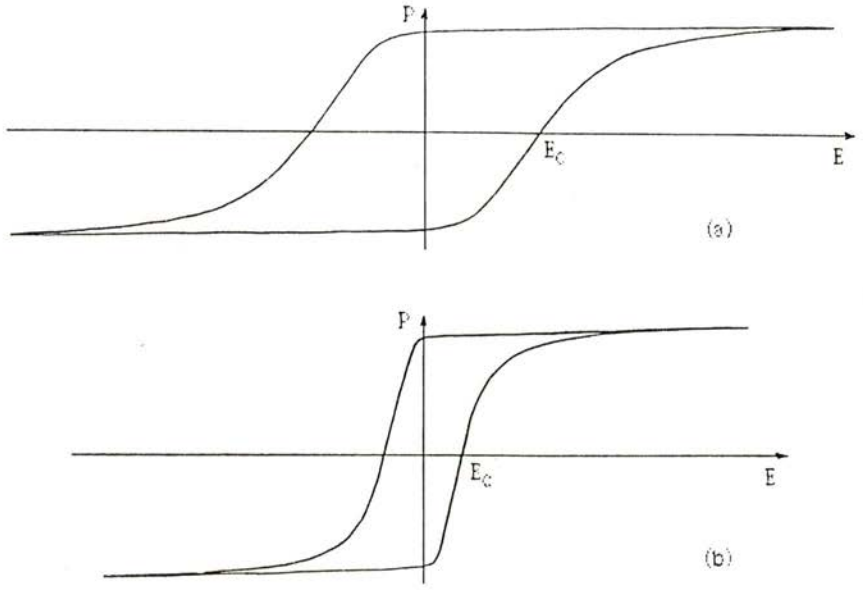

Fig. 7 — Hysteresis loops relating to sample 1 (a) at temperature T = 319.75K and sample 3 (b) at temperature T = 319.85K. The coercive fields are E_c (a) = 3,9 kV/cm and E_c (b) = 0.7 kV/cm, respectively.

field value of sample 3 shows the good condition of this sample's surface, the higher one obtained for sample 1 is surely a consequence of the excessive temperature which the sample attained when it was prepared. This is believed to cause the formation of viscous superficial layers which on cooling have a different behaviour from that of the initial crystal [9].

The spontaneous polarization P_s obtained from hysteresis loops, in both samples, is shown in Fig. 6 with the corresponding results obtained from pyroelectric measurements. In sample 1, the coincidence of the polarization curves obtained with both methods is somewhat surprising. As a matter of fact, we believe that the polarization values obtained from hysteresis loops should be higher than the pyroelectric ones, because of the inducing effect of the applied electric field.

We found that the ε_r^{-1} data could be satisfactorilly fitted to the expression:

$$\varepsilon_r^{-1} \propto |T - T_0| \ , \ T > T_0 \ ; \ \varepsilon_r^{-1} \propto |T_0' - T|^{\gamma'} \ , \ T < T_0' \ .$$

with $\gamma = \gamma' \simeq 1.0$. These values for γ and γ' are the ones predicted by Landau's theory. However in this theory $T_0 = T_0'$, which is not the case in our experiments (Fig. 2), where we obtained $|T_0 - T_0'| < 0.28$K.

The critical exponent β associated with the spontaneous polarization ($P \propto |(T - T_c)/T_c|^{\beta}$) was calculated choosing the critical temperature T_c as the one corresponding to the maximum value of the pyroelectric coefficient. This value is close to the temperature corresponding to the maximum of the dielectric constant versus temperature (Table I). The β values for samples 1 and 3 obtained from the pyroelectric effect as well as from

TABLE III — β values for samples 1 and 3 obtained both from the pyroelectric effect and from hysteresis loops.

Number of sample	T_c (K)	$\beta \pm 0.02$ obtained from	
		Pyroelec. effect	Hysteresis loops
1	322.73	0.49	0.52
3	322.87	0.48	
	322.95	0.50	

hysteresis loops (Table III) are coherent with the predicted Landau value of 1/2.

It should be emphasized that the choice of T_c has a significant influence in the β value, as can be seen in Table III for sample 3.

The critical exponent δ is obtained from hysteresis loops. It relates the polarization with the applied electric field at T_c ($E \propto P^{\delta}$, for $T = T_c$). The values obtained for sample 3, at temperatures near T_c are represented in Table IV, and are comparable to the predicted Landau value of 3. The deviations from this value can be attributed to the difference between the temperature at which δ is calculated and T_c .

TABLE IV — δ values for temperatures near $T_c = 322.87$ K, concerning sample 3

T (K)	δ
322.73	3.02
322.60	2.90
322.46	3.14

Following Gonzalo [18, 19] we checked for scaling behaviour and considered the rescaled values of polarization p and electrical field e ,

$$p = P / |(T - T_c) / T_c|^{\beta} , \quad e = E / |(T - T_c) / T_c|^{\beta\delta}$$

where P is the polarization and E is the electric field corresponding to a point in a hysteresis loop at temperature T , T_c is the critical temperature, $\beta = 1/2$ and $\delta = 3$. We plotted ln p vs. ln e in the temperature range $|T - T_c| < 0.5$K in Fig. 8, for sample 3. These results are in a quite reasonable agreement with those previously determined by Gonzalo [16]. The differences obtained must result from the fact that the temperatures of the hysteresis loops we have considered were not near enough to T_c .

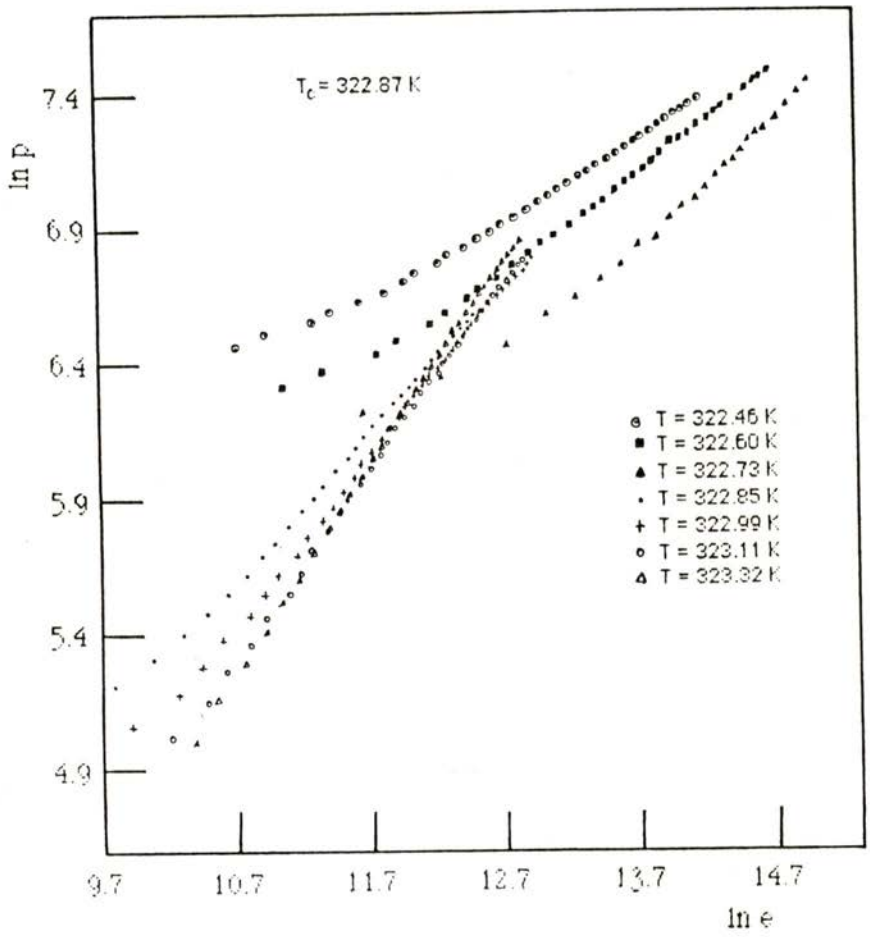

Fig. 8 — ln p vs. ln e relating to sample 3, for the indicated temperatures, with $T_c = 322.87$K.

4 — CONCLUSIONS

The main interest of this work lies in the presentation of a systematic and quite complete study of experimental macroscopic properties of triglycine sulfate. We have shown that: (i) the dielectric constant has finite values at the transition temperature in all the samples studied; (ii) the value for the ratio m_1 / m_2 is not in agreement with the value 2 predicted by Landau theory and the difference cannot be caused by domain clamping; (iii) the

values of the critical exponents γ, γ', β and δ agree with those predicted by the Mean Field Theory and verify the predicted scaling relations; (iv) the rescaled values of the polarization and field can follow an equation of state; (v) the relaxation of domains in TGS does not follow an exponential law.

A study regarding the relaxion of domains in TGS at different temperatures near T_c is presently in progress.

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