

## PECULIAR ASPECTS IN FERROELECTRIC TRANSITION OF TRIGLYCINE SULPHATE CRYSTAL

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**Abstract.** *Fundamental dielectric parameters of pure triglycine sulphate crystals were determined versus temperature (-120/+50 °C) and frequency (1 Hz-10 MHz), in the ferroelectric phase, following a special temperature program. Essential ferroelectric parameters, relaxation time and Cole-Cole parameters were estimated on a large temperature range. It has been found three relaxation processes in the approximate frequency ranges: LOW (~10<sup>2</sup> Hz), MEDIUM (~10<sup>4</sup> Hz) and HIGH (~4·10<sup>5</sup> Hz). The HIGH relaxation seems to be related to the fundamental effect of long range interaction specific to ferroelectric effect, while the LOW relaxation is related the ferroelectric domain interaction. The MIDDLE relaxation do not appears to have a specific physical support, being rather an interaction of the previous ones through the lattice dynamic.*

**Keywords:** triglycine sulphate, ferroelectric transition, dielectric relaxation vs. frequency and temperature, relaxation time, activation energies

### 1. Introduction.

Ferroelectric crystals and ceramics have important technological applications. Triglycine sulphate crystal (TGS) was intensively studied for its fundamental properties and important technological applications, particularly high sensitivity pyroelectric detectors [1, 4]. We have earlier presented single crystal growth conditions and important ferroelectric properties [5, 7]. Relaxation phenomena we have also extensively studied [8, 13].

In this paper we present original data obtained based on the concept of Cole-Cole representation [14] and the relaxation time for the three relaxation processes, we have found. Activation energies shall be estimated from Arrhenius representations and the nature of the relaxation processes shall be discussed.

### 2. Experimental.

Pure TGS crystals were grown from solutions prepared from purified substance, synthesized and purified by fractional recrystallization [8]. Crystals were grown in a thermostated oven, by slow solvent evaporation at 54 °C, in paraelectric phase. This way, it was avoided the lattice distortions which usually are involved in growth of crystals in ferro phase, due to defects and mechanical tensions

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generated by ferroelectric domains present during growth. Samples were prepared by cleavage perpendicular on the “b” ferroelectric axis. Polished sample of about  $0.8 \text{ cm}^2$  surface and  $\sim 1 \text{ mm}$  thickness were silver paste painted as electrodes.

Measurements were automatically made with Alpha-A Novocontrol dielectric spectrometer. The temperature control of the sample was ensured by the system with a nitrogen stream, whose temperature was electronically monitored, according to the temperature program. The temperature was increased from RT to  $65 \text{ }^\circ\text{C}$ , where it was kept constant for 30 minutes in order to eliminate the space charge from the sample eventually accumulated during the first cross-up of the Curie point. Then, measurements were made while the temperature was decreased down to  $-120 \text{ }^\circ\text{C}$  at a pace of  $0.6^\circ\text{C}/\text{min}$  and then following a complex temperature program [8].

Both component of permittivity were registered on the frequency range  $1 \text{ Hz} \div 10 \text{ MHz}$ , considering five equidistant measurements points in log scale, on every frequency decade. Than only  $65 \text{ }^\circ\text{C}$  to  $-120 \text{ }^\circ\text{C}$  temperature range were explored, crossing down the Curie point ( $\sim 49 \text{ }^\circ\text{C}$ ). The experimental data were analyzed using programs associated to the dielectric spectrometer (task accomplished by Dr. C.-P. Ganea). Then, some ferroelectric parameters were analyzed and activation energies found, in order to have a solid interpretation of the data.

### 3. Results.

Several representations of permittivity components  $\epsilon'$  and  $\epsilon''$  vs. frequency and temperature we have checked. On the frequency range  $1 \div 10^7 \text{ Hz}$ , three relaxation processes previously detected [8, 15, 16] were confirmed again. Some other original aspects shall be further considered.

#### 3.1. Frequency dependence of permittivity components.

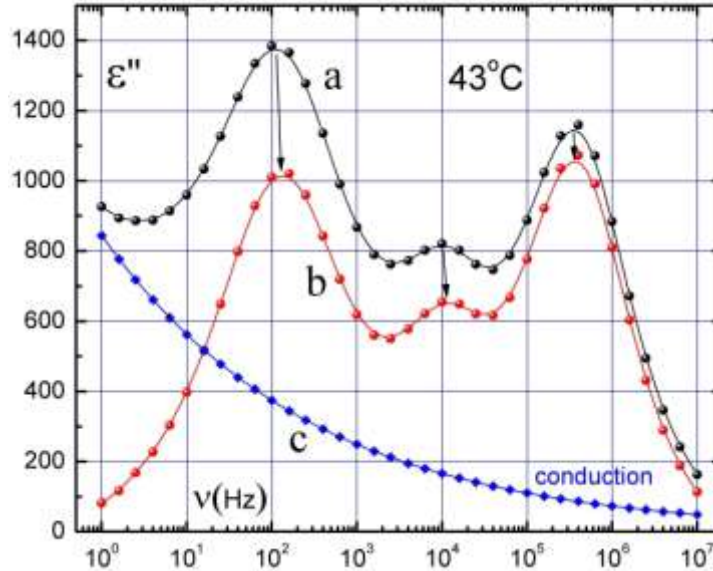
The real and the imaginary components of permittivity in the Debye concept are:

$$\epsilon' = \epsilon_\infty + \frac{\epsilon_{st} - \epsilon_\infty}{1 + \omega^2 \tau_\epsilon^2} \quad (1)$$

$$\epsilon'' = \frac{\omega \tau_\epsilon (\epsilon_{st} - \epsilon_\infty)}{1 + \omega^2 \tau_\epsilon^2} + \frac{\sigma}{\epsilon_0 \omega} \quad (2)$$

Here  $\epsilon_\infty$  and  $\epsilon_{st}$  are the extreme values of the real component of permittivity in Cole-Cole [17] representation (see below),  $\tau_\epsilon$  the relaxation time of dielectric constant and  $\sigma$  the conductivity. In eq. (2) the first term is related to the dielectric losses and the second one to conduction losses.

In fig. 1 we present the frequency dependence of the imaginary component of permittivity at 43 °C in the ferroelectric phase (a). The decomposition was realized by a fitting program of the spectrometer according to a similar eq. (2).



**Fig. 1.** Frequency dependence of  $\epsilon''$  the imaginary components of permittivity at 43 °C. a/ component with conduction losses, b/ without conduction, c/ conduction losses - see eq.(2).

The three maxima of the components “a” and “b” in fig. 1 suggest three relaxation processes as shall be further discussed. The relaxation time is related with this maxima as  $\omega \cdot \tau_\epsilon = 1$ , i.e.  $\tau_\epsilon = 1/2\pi\nu$  and depend on the temperature in a specific mode, according to the considered type of the relaxation process. The frequency values of the maxima of curves “a” and “b” in fig. 1 are not substantially different, although the conduction term “c” has an essential contribution at lower frequencies (more than 90 % at 1 Hz and almost 30 % at 1 kHz). Thus, the relaxation time for the three relaxation processes is not essentially affected by the sample conduction.

### 3.2. Cole-Cole representation and ferroelectric parameters.

In fig. 2 we present  $\epsilon''$  versus  $\epsilon'$  in two versions with and without conduction terms, according to Cole-Cole concept [17]. At “HIGH” and at “LOW” frequencies the arcs Cole-Cole could be drawn quite safely. However, the “MIDDLE” one, although clearly discerned, has large zones of superposition with the previously mentioned ones. Besides, at frequencies lower than about 50 Hz, although the conduction term was subtracted in fig. 2.b, the tail at lower frequencies (10 to 1 Hz) is still visible. Some other effect, like space charge, seems to be effective at such frequencies.

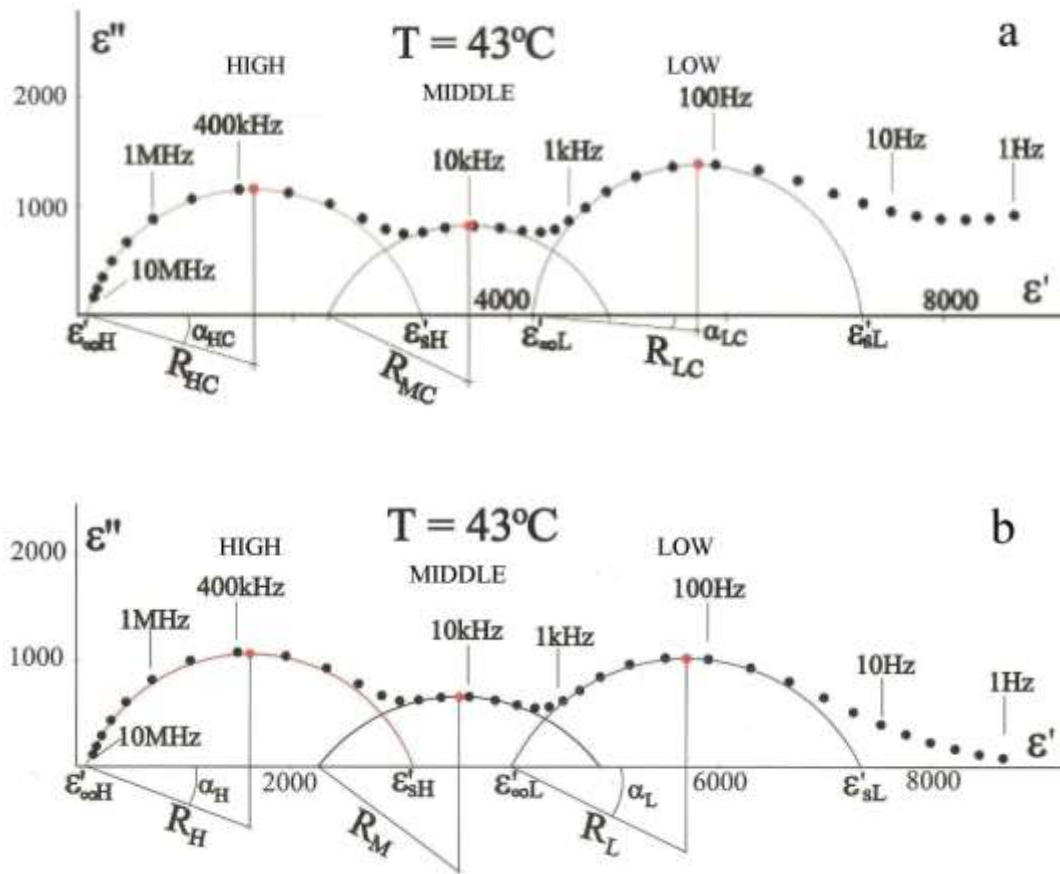


Fig. 2. Cole-Cole representation of dielectric components:  
 a – with conduction components;  
 b – without conduction components.

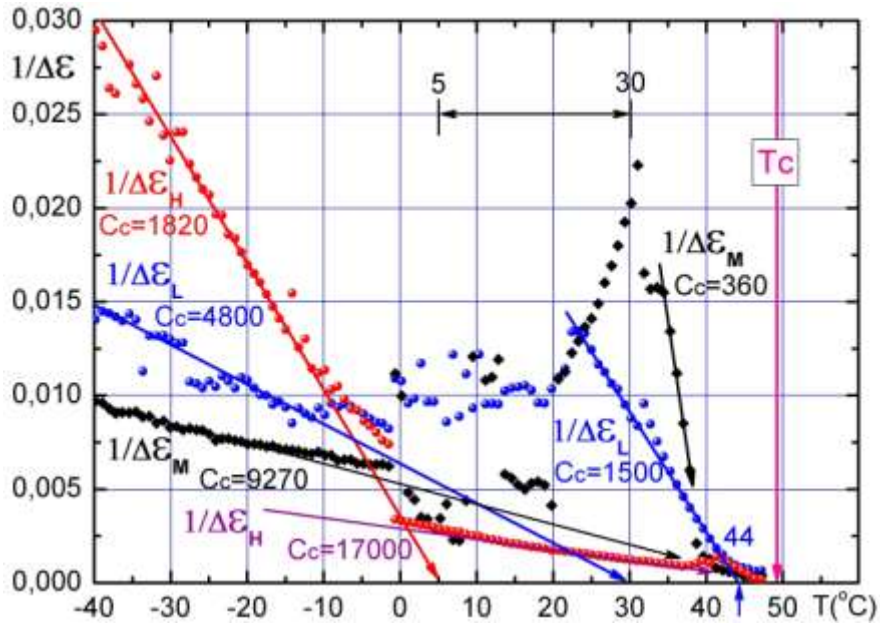
Other parameters like  $\epsilon_\infty$  and  $\epsilon_{st}$  and consequently  $\Delta\epsilon = \epsilon_{st} - \epsilon_\infty$  are not much affected.

However, the radius  $R$  of the arcs Cole-Cole and the  $\alpha$  parameters are substantially changed especially for “MIDDLE” and “LOW” relaxation effects.

### 3.3. Checking the Curie-Weiss law of the parameter $\Delta\epsilon = \epsilon_{st} - \epsilon_\infty$ .

The well-known Curie-Weiss law  $\epsilon = C/|T-T_0|$  which usually is checked at 1 kHz around the Curie point of the second ferroelectric transitions, has in fact no basic physical concept to be supported.

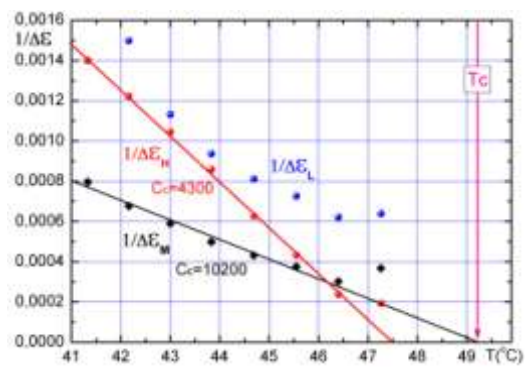
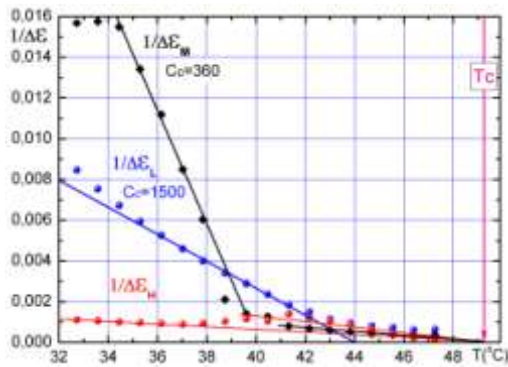
We have earlier found this law applies also for other frequencies and the Curie Constant “ $C$ ” has a peculiar dependence on the frequency [18].



**Fig. 3.** The Curie-Weiss law for the reverse of  $\Delta\epsilon = \epsilon_{st} - \epsilon_{\infty}$  corresponding to High (H), Middle (M) and Low (L) relaxation processes in ferro phase of TGS.

**Table 1.** Constant values C and  $T_0$  in the C-W law of  $\Delta\epsilon = \epsilon_{st} - \epsilon_{\infty}$  (figs. 3-5)

Temp. (°C)	HIGH		MIDDLE		LOW		Fig.
	C const.	$T_0$ (°C)	C const.	$T_0$ (°C)	C const.	$T_0$ (°C)	
-40 ÷ 0	1820	5	<b>9270</b>	$T_0 (\approx 49)$	4800	30	<b>3</b>
32 ÷ 42	---	$T_0 (\approx 49)$	360	<b>40</b>	1500	<b>44</b>	<b>4</b>
41 ÷ $T_c$	4300	47.5	<b>10200</b>	$T_0 (\approx 49)$	---	---	<b>5</b>



**Fig. 4.** Curie-Weiss law, detail from fig. 3. **Fig. 5.** Details from in fig.4, close to Curie point.

It was found that the ratio of the Curie constants in para and in ferro phase does not have the value 2, as predicted by the thermodynamic and Landau theory of ferroelectrics. In the cooling process, this ratio has a spectacular change around  $5 \cdot 10^5$  Hz (see fig. 8 in ref. [18]) and we notice this frequency is close related with the relaxation time  $\tau = 1/2 \pi \cdot 5 \cdot 10^5 = 3.2 \cdot 10^{-7}$  sec which correspond to the “HIGH” relaxation of TGS crystal in fig. 1.

Here we check the validity of Curie-Weiss law for the parameter  $\Delta\varepsilon = \varepsilon_{st} - \varepsilon_{\infty}$ . On a large temperature range, we present this dependence in figs. 3 and near the transition point in figs 4 and 5.

It is quite surprising that at large distances from transition point, between  $-40$  °C and  $0$  °C, the Curie-Weiss law apparently apply to all three relaxation mechanism HIGHER, LOWER and MIDDLE (see table 1). However, the Curie point  $T_0$  shown by the relaxation mechanisms (except the MIDDLE one) do not correspond to the transition point ( $\approx 49$  °C). We note that in the region  $5-30$  °C the LOWER and the MIDDLE relaxation shows an instability in the measuring process (fig. 3).

In the region  $32 \div 42$  °C there are another set of points obeying the Curie-Weiss law with some other characteristics. The MIDDLE and LOW relaxations points to  $40$  °C and  $44$  °C as the Curie points. This temperatures seems to be related with some turning points in the relaxation time versus temperature of HIGH and LOW relaxations (see figs. 8, 9 and 10 in ref [8]).

In the region  $42$  °C and the transition point the HIGH and LOW relaxation obey the Curie-Weiss law, while HIGH relaxation points to  $47.5$  °C as the Curie temperature.

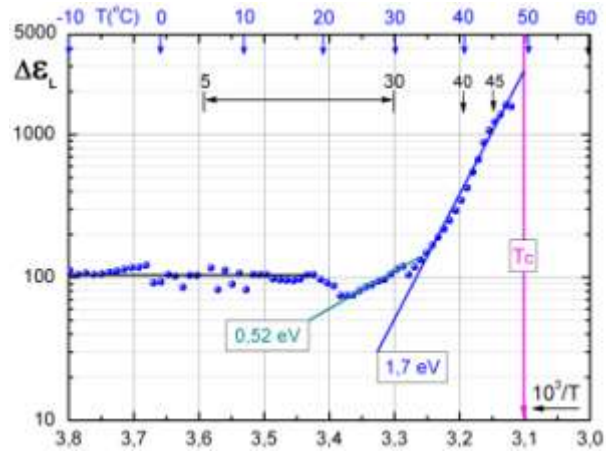
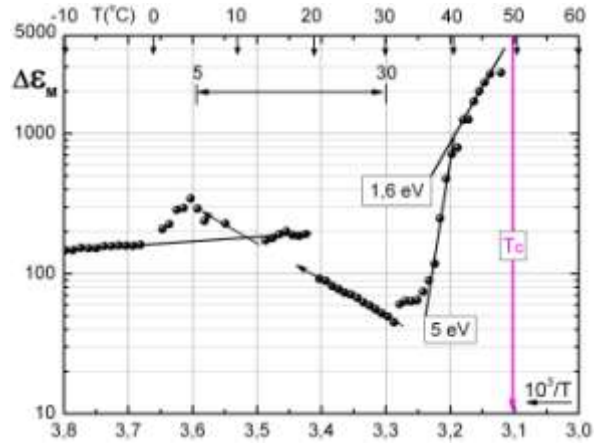
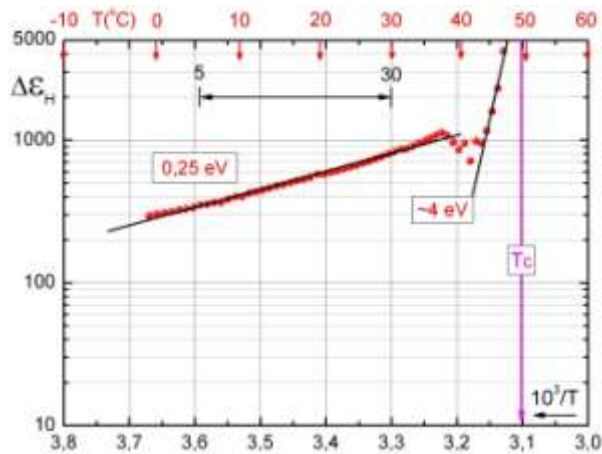
### 3.4. Checking the activation energy of $\Delta\varepsilon = \varepsilon_{st} - \varepsilon_{\infty}$ .

The significance of the extreme values of  $\varepsilon'$  in the Cole-Cole representation are:  $\varepsilon_{st}$  the estimated value at the lowest frequency and  $\varepsilon_{\infty}$  the estimated value at the highest frequency of the specific relaxation mechanism. The extreme values of the MIDDLE mechanism are the less precisely estimated (see fig. 2).

In order to see if  $\Delta\varepsilon$  have a thermal activation character; we have drawn in figs. 6, 7 and 8 the Arrhenius representation for the three relaxation mechanism.

The LOW relaxation mechanism in fig. 6 shows an activation energy of  $1.7$  eV, (i.e. about  $60$   $k_B T$  near the Curie point, or  $\sim 40$  kcal/mole), which is quite high.

The MIDDLE relaxation shows a similar value of the activation energy of  $1.6$  eV. This figure suggests that at least on a narrow temperature interval  $40 \div 45$  °C both relaxations are related.

Fig. 6. Arrhenius data of  $\Delta\epsilon_L$ .Fig. 7. Arrhenius data of  $\Delta\epsilon_M$ .Fig. 8. Arrhenius data of  $\Delta\epsilon_H$ .

The HIGH relaxation mechanism apparently has the activation energy of  $\sim 4$  eV on the temperature interval  $40 \div 46$  °C which is unreasonable high. This value suggests the mechanism is not thermally activated, but rather is related with the long distance interaction energy, typical for ferroelectric phenomena.

### 3.5. The relaxation time.

The relaxation time is an important parameter used to characterize thermally activated mechanism of physical processes. In the dielectric spectroscopy the relaxation time can be found by two equivalent procedures. In  $\varepsilon''(\nu)$  – the frequency representation (fig. 1), the maxima values correspond to the condition  $\omega \cdot \tau = 1$ , i.e.  $\tau = 1/2\pi\nu$  and  $\tau(T)$  can be found on a large temperature range. In the Cole-Cole representation the condition for maxima of  $\varepsilon''$  is associated with the relaxation frequency and with  $\tau_\varepsilon$  the corresponding relaxation time (see fig. 2). The estimated  $\tau_\varepsilon$  values are not much affected if the conduction term (“c” in fig. 1, see also eq. (2)) is considered or not.

In fig.1 the relaxation time is associated with the following relaxation frequencies:  $\nu_{\text{LOW}} \approx 10^2$  Hz,  $\nu_{\text{MID}} \approx 10^4$  Hz and  $\nu_{\text{HIGH}} \approx 4 \cdot 10^5$  Hz, but generally it might cover many order of magnitude.

The LOW relaxation time is presented in fig.9, in Arrhenius coordinate. The activation energy of 0.6 eV has been estimated on about 80°C temperature interval. This figure is fair close to 0.7 eV, figure we have estimated [8] on the temperature interval  $0 \div 45$  °C.

The MIDDLE relaxation time in fig. 10, also presented in Arrhenius coordinate, has 0.68 and 0.60 eV activation energy on  $5 \div 30$  °C. Although on this temperature interval LOW and MIDDLE parameters shows instability (see figs. 6 and 7), the activation energy of both relaxation are very close. This fact suggests, that both relaxation mechanisms are some way related.

On the temperature interval  $30 \div 40$  °C the activation energy of the MIDDLE relaxation time  $\tau_M$ , substantially increases to more than 2 eV). This do not seem to correlate to other relaxation, may be except HIGH relaxation.

The HIGH relaxation time  $\tau_H$  does not have relevant temperature dependence in Arrhenius coordinate. It seems this parameter is almost constant between 0 °C and the Curie point. More details can be found in ref. [8]. It was shown that between 40 and 45 °C,  $\tau_H$  has a non-Arrhenius behavior, while between 45 °C and Curie point, surprisingly fall down more than one order of magnitude (fig. 10 in ref [8]). In fig. 11 there is unexpected break of  $\tau_H$  around 0 °C and non-Arrhenius temperature dependence on the temperature interval  $-40$  °C and 0 °C.



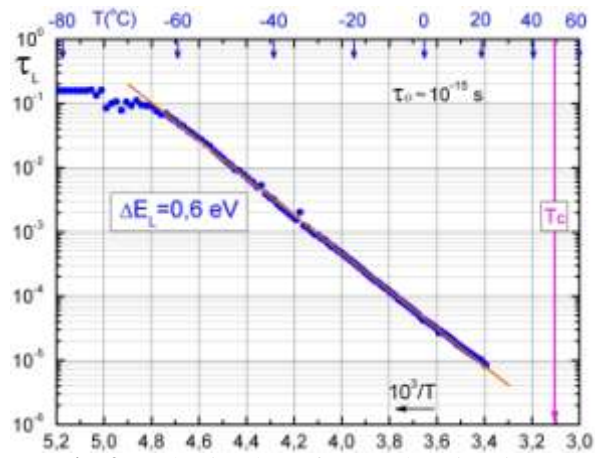


Fig. 9. Arrhenius data of Low relaxation time.

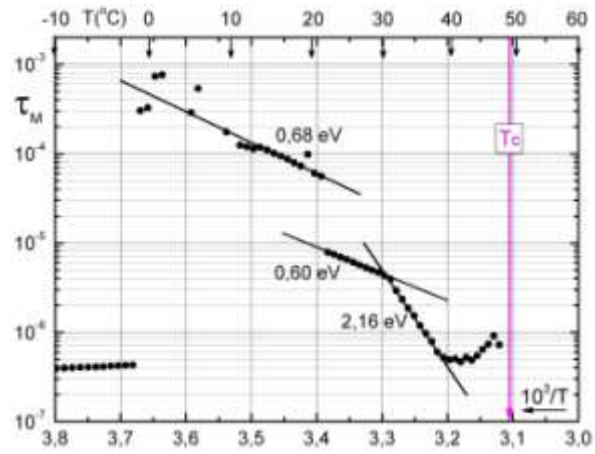


Fig. 10. Arrhenius data of Middle relaxation time.

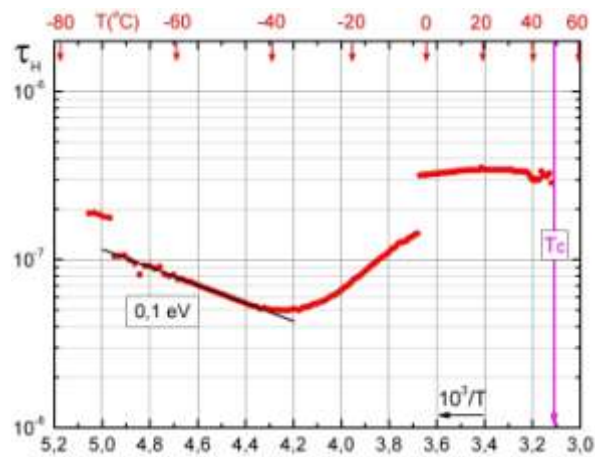


Fig. 11. Arrhenius data of High relaxation time.

#### 4. Discussions.

Temperature and frequency dependence of important ferroelectric parameters of TGS were analysed. The frequency dependence of  $\epsilon''$  and Cole-Cole representations allowed to estimate the relaxation time for the three distinct relaxation effect.

The parameter  $\Delta\epsilon = \epsilon_{st} - \epsilon_{\infty}$  representing values at the extreme frequencies of the real component of permittivity for the three relaxations, was checked as  $1/\Delta\epsilon = f(T)$  for a Curie-Weiss temperature dependence. Surprisingly, the HIGH, MIDDLE and LOW relaxations, between  $-40$  °C and  $0$  °C, points to genuine Curie-Weiss relations were transition does not really exist (fig.3). Only MIDDLE relaxation seems to have the “Curie point” at  $\sim 49$  °C. The other relaxations have “Curie point” approximately at  $5$  °C and  $30$  °C. This fact quite strange was not presented in the literature yet.

In the temperature range  $5\div 30$  °C a sort of disorder of only LOW and MIDDLE relaxation take place. In the range  $20\div 30$  °C MIDDLE relaxation has non-Arrhenius temperature dependence (fig.3). On the other hand, at the limit of zero Celsius the HIGH relaxation has dramatically changed the slope of  $\Delta\epsilon_H$ . Between  $0\div 40$  °C this relaxation points to real Curie point and has the Curie constant  $C_c \approx 17000 \text{ grd}^{-1}$ , unusually high.

In the range  $32\div 42$  °C,  $1/\Delta\epsilon$  of MIDDLE and LOW relaxation show the Curie point around  $40$  and  $44$  °C (fig. 4) and this seems to be reference temperatures in the Raman spectra of TGS [19].

Close to the Curie point (between  $41\div 49$  °C),  $1/\Delta\epsilon$  of the HIGHR relaxation, points close to the “Curie” point (about  $47.5$  °C in fig. 5). The MIDDLE one seems to be the only relaxation which points exactly to the real Curie point of  $\sim 49$  °C.

Crossing down the Curie point the permittivity increases considerably versus the values measured, crossing up run. A huge number of very small domains appear and there is a long evolution which changes their topography [20]. The increase of permittivity is related with the domain wall oscillation produced by the small measuring electric field applied ( $\leq 1$  V/cm). The relaxation time of the ferroelectric domains (typical for LOW relaxation,  $\tau_L$ ), found here from permittivity measurements has the activation energy  $0.6$  eV and  $0.7$  eV found in ref. [8].

It might be supposed that  $\Delta\epsilon$ , we have jointly measured here, is also thermally activated. The associated activation energy of  $1.7$  eV, we have estimated in fig.6 is however larger than expected, but still reasonable.

In the temperature range  $40\div 45$  °C the activation energy of the MIDDLE relaxation ( $\Delta\epsilon_M$ ) is  $1.6$  eV and suggest this “intriguing” relaxation might be related

with the LOW relaxation here. At temperatures lower than 40 °C the apparent activation energy of 5 eV is unexpectedly high, but difficult to be directly related with the activation energy 4 eV of  $\Delta\epsilon_H$  (figs. 7 and 8).

The temperature dependence of the relaxation time  $\tau(T)$  is very important in establishing the nature of every relaxation process. The activation energy 0.6 eV (fig. 9), estimated on a large temperature range (more than 80 °C) for LOW relaxation is in fair agreement with earlier estimations [8]. This suggests the dynamics of the ferroelectric domains are really thermally activated. However, between 45 °C and the Curie point, the LOW relaxation time  $\tau(T)$  has a non-Arrhenius temperature behavior (see fig. 9 in ref [8]). This might suggest the direct influence of transition do not extend in ferro phase more than about 4 °C down the Curie point.

On the “unstable” 5÷30 °C temperature range the MIDDLE relaxation time has activation energy 0.60 - 0.68 eV, close to those of LOW relaxation, to whom might be related. We note than between 45 °C and Curie point,  $\tau_M$  shows also a non-Arrhenius behavior.

The HIGH relaxation time  $\tau_H$  is almost constant on 0 ÷40 °C temperature range. It is quite clear this mechanism of relaxation is related with a long distance interaction characteristic to ferroelectric order. It has also non-Arrhenius temperature dependence near the Curie point.

### Conclusions.

1. The parameter  $\Delta\epsilon = \epsilon_{st} - \epsilon_{\infty}$  (of several relaxations) follows a sort of “Curie-Weiss” law in the temperature range (-40) ÷ (0) °C, wich indicate several “Curie” points between 5°C and the real Curie point (~ 49 °C). On the temperature range (5) ÷ (30) °C there is a sort of disorder in measuring the parameter  $\Delta\epsilon$  of LOW and MIDDLE relaxation.
  2. The  $\Delta\epsilon$  parameter apparently has the Arrhenius activation energy of 1.7 eV for LOW and 1.6 eV for MIDDLE relaxation, on the temperature range 40 ÷ 45 °C. Data suggest both relaxations are related in some way on this temperature range.
  3. The activation energy of the relaxation time of LOW and MIDDLE relaxations have similar values (0.6 – 0.7 eV) on the temperature range (0) ÷ (30) °C. These data suggest a similar mechanism related with the dynamic of ferroelectric domain relaxation.
  4. The LOW and MIDDLE relaxations show, jointly to some previous data [8], to have a non-Arrhenius temperature dependence on the temperature range 45 °C and  $T_{Curie}$ . This seems to be typical for the temperature interval, not larger than approximately 4 °C, of the influence of transition down the Curie point.
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5. The HIGH relaxation time appears as not temperature dependent in the range (0) ÷ (40) °C and suggests this mechanism of relaxation is directly related to the long distance order, typical to ferroelectrics.

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