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# Investigation of the pyroelectric and piezoelectric properties of triglycine sulphate single crystals containing organic molecules

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**Abstract.** The pyroelectric coefficient and the piezoelectric modulus of triglycine sulphate (TGS) single crystals doped with d-l-alanine, orthonitroaniline, paranitroaniline or aniline molecules has been measured from room temperature up to the transition point. The data are compared with those which we have previously obtained on pure TGS. A noticeable increase in the value of the pyroelectric coefficient of the doped samples over the whole temperature range is observed. A significant pyroelectric signal is still detected several degrees above the transition point of pure crystals. The spontaneous polarisation is calculated using data for the measured pyroelectric current. The piezoelectric modulus of the doped crystals reaches its maximum value at a temperature lower than the Curie point of pure TGS before it decreases steadily to zero. A relation between the piezoelectric modulus and the temperature just before the maximum value is deduced. The role of the internal bias created in the crystal after doping is also discussed.

## 1. Introduction

Single crystals of triglycine sulphate (TGS) are considered to be one of the most suitable materials for pyroelectric detectors (Keve 1975). However, a drawback arises from the observed spontaneous depolarisation with time for these crystals. This behaviour may be reduced by doping TGS crystals with molecules of the l-alanine (Löck 1971, Tylczyński 1981), the nitroaniline group (Krajewski and Breczewski 1980) or aniline (Eisner 1978). The dopant molecules are thought to form distorted areas which act as polar centres. A sufficiently high concentration of these centres will result in a self bias on the crystal which can polarise the intervening matrix of pure TGS. The internal bias in l-alanine-doped TGS crystals was found to be changeable near the transition tending to zero at a temperature several degrees above the Curie point  $T_c$  of pure TGS (Martinez *et al* 1983).

Doping TGS with l- $\alpha$ -alanine strongly reduces the dielectric permittivity,  $\epsilon_{22}$ , and increases the spontaneous polarisation,  $P_s$ , of TGS crystals (Keve 1975). On the other hand, Tylczyński (1981) reported a decrease in the maximum value of  $\epsilon_{22}$  and also a decrease in  $P_s$ , the latter observation being in contrast to the observations of Keve (1975). Moreover, the variations in both  $\epsilon_{22}$  and  $P_s$  are dependent on the l-alanine content in the crystal which is about  $\frac{1}{20}$ – $\frac{1}{30}$  of that in the solution of growth (Bye *et al* 1972). However, TGS crystals highly doped with l- $\alpha$ -alanine cracked easily while preparing the thin plates required for fabrication of the detectors (Keve *et al* 1971).

The pyroelectric coefficient increased while  $\epsilon_{22}$  decreased for TGS crystals containing  $3 \times 10^{-3}$  weight% of paranitroaniline (PNA), orthonitroaniline (ONA) or metanitroaniline (MNA) molecules (Krajewski and Brezczewski 1980). The change in both  $\epsilon_{22}$  and  $P_s$  is a function of the dipole moment of the dopant molecule. Accordingly, a maximum increase of about 40% in the sensitivity of the detection parameters of TGS was achieved in the case of doping with PNA.

The piezoelectric properties of pure TGS have been studied by several authors. Baják (1975) using the surface excitation of ultrasonic waves related the piezoelectric stress constant  $e_{23}$  to temperature through a relation of the form  $e_{23} = K_{23} (T_c - T)^{-1}$  where  $T_c = 49.6^\circ\text{C}$  and  $K$  is a constant. Publications which deal with piezoelectric properties of TGS crystals doped with organic molecules are scarce in the literature. This may be due to the difficulty of growing good crystals of TGS doped with organic molecules for such study.

d-l-alanine as a dopant in TGS crystals has not been tried so far. According to its character, we hope that this dopant will give TGS some interesting properties. Therefore this study will be the first aim of the present work. The second goal is a comparative study to investigate the role of organic dopant molecules of different character in identical concentration in the solution of growth and with nearly the same growth conditions on pyroelectric and piezoelectric properties of TGS crystals.

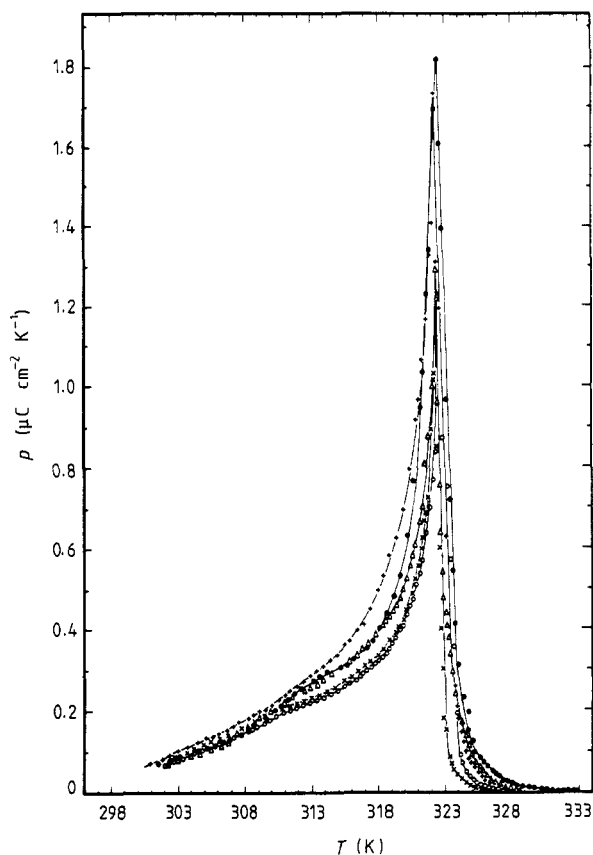
## 2. Experimental

Single crystals for the present investigation were grown from saturated aqueous solutions by the temperature lowering method. The concentration of the dopant molecules in the solution of growth was 2 weight%. Natural—as grown—small pure crystals were used as seeds in all the cases. All crystals were grown using nearly identical growth parameters. However, some minor changes in the regime of crystallisation were performed during growth owing to the difference in the physical and chemical character of the dopant molecules. The temperature of the initial crystallisation was 319 K and the temperature lowering rate was initially  $0.1 \text{ K d}^{-1}$  increasing linearly to  $0.2 \text{ K d}^{-1}$ . d-l-alanine, orthonitroaniline (ONA), paranitroaniline (PNA) or aniline were chosen to be the dopant molecules for the present study. Well developed planes, transparent and flawless in most parts of the crystals were obtained in all cases.

Samples in the form of thin plates, about  $8 \times 8 \times 1\text{--}2 \text{ mm}^3$  were prepared with the smallest edge parallel to the ferroelectric  $b$  axis. Conducting silver paste was painted on the two opposite sides perpendicular to the  $b$  axis. A special sample holder in an evacuated pyrex glass tube was used (vacuum of about  $10^{-3}$  Torr).

The temperature was measured and controlled with an accuracy of about 0.05 K using a chromel–alumel thermocouple. The measurements of the pyroelectric current were performed while heating at a constant rate of about  $3.47 \times 10^{-3} \text{ K s}^{-1}$  by the short-circuit current method using a Keithley electrometer type 610 C. The error in the measured values did not exceed 3%. The piezoelectric studies were performed by the resonance–antiresonance method. The maximum and minimum currents in the circuit were detected using an AC millivoltmeter (Philips type PM 2454, 10 Hz–12 MHz). The maximum error in computing the piezoelectric modulus is less than 3%.

Before initiating each series of measurements, an electric field of about  $1 \text{ kV cm}^{-1}$  from a DC power supply (Pasco model 1030 A) was applied to the sample at about 335 K for 1 h. Later, while the electric field was acting the temperature of the sample was



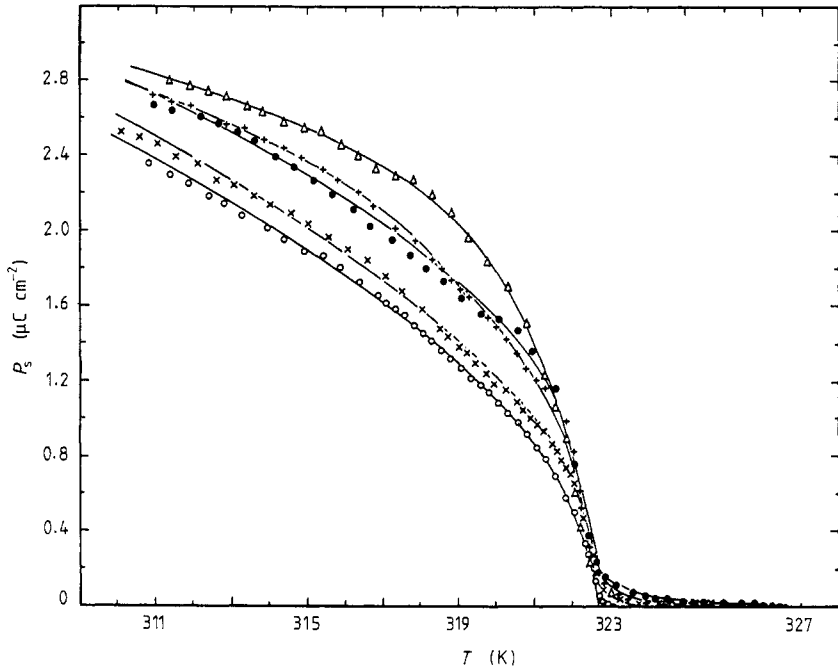
**Figure 1.** The temperature dependence of the pyroelectric coefficient of TGS crystals doped with organic molecules. The results for the pure sample are also included. ○, pure TGS; ●, d-l-alanine-doped TGS; △, ONA-doped TGS; ×, PNA-doped TGS; +, aniline-doped TGS.

decreased at a rate of  $0.5 \text{ K h}^{-1}$  in the region of the phase transition and  $2 \text{ K h}^{-1}$  in the regions far from the transition point.

### 3. Results and discussion

#### 3.1. Pyroelectric coefficient

The temperature dependence of the pyroelectric coefficient,  $p$ , of TGS crystals doped with d-l-alanine, ONA, PNA or aniline is shown in figure 1. The results for the pure sample are also included for the sake of comparison. From the measurements it was observed that the temperature for  $p_{\text{max}}$  of the doped samples is shifted towards lower temperatures, the maximum shift is about  $0.5 \text{ K}$  in the case of the aniline-doped sample. All the doped samples exhibited higher pyroelectric coefficient in comparison with the pure one. An increase in the peak value of  $p$  of about 49%, 2%, 6% and 44% can be observed in the case of d-l-alanine-, PNA-, ONA- and aniline-doped samples respectively. The observed increase in pyroelectric coefficient of TGS crystals after doping can be related to the bias field created in the crystal because of the dopant molecules. The appearance of an internal



**Figure 2.** Spontaneous polarisation  $P_s$  of doped TGS crystals between room temperature and the transition point. The results for pure crystals are also presented for the sake of comparison.  $\circ$ , pure TGS;  $\bullet$ , d-l-alanine-doped TGS;  $+$ , ONA-doped TGS;  $\times$ , PNA-doped TGS;  $\triangle$ , aniline-doped TGS.

bias in TGS was reported for crystals grown in the ferroelectric phase even in the absence of dopants (Shaulov and Simhony 1976). Accidental impurities in the solution of growth may be responsible for the internal bias since the lower the growth temperature the higher the internal bias detected in the crystal (Tsedrik and Zaborowski 1976). As shown by Jaśkiewicz (1965) the bias is generated because of the electric charges occurring on domain boundaries which slightly influences the coercive field of the crystal. In the literature, values for the bias field in pure TGS crystals between 3 and 15  $\text{kV m}^{-1}$  were reported.

Alanine is an amino-acid-like glycine but with a  $\text{CH}_3$  group replacing one of the  $\alpha$ -hydrogen atoms. Keve *et al* (1971) postulated that the similarity is sufficient for aniline to be substituted at glycine sites in doped TGS crystals. Replacing a glycine molecule by a larger molecule should introduce local strains. Also, for alanine two forms exist d- and l-alanine—each is the mirror image of the other. If a 'racemic' mixture of equal quantities of d- and l-alanine is incorporated in TGS, then crystals with large permanently polarised domains are formed below the Curie temperature, some with a given direction, others with the opposite one. The existence of this limited number of domains in the entire crystal may be a reason for the stabilisation of the structure against the polarisation reversal process. Such a stabilisation may be responsible for the high pyroelectric signal detected for the d-l-alanine-doped sample in comparison not only with the pure case but also with the doped ones.

The nitroaniline molecule exists in three forms: PNA, MNA and ONA. The difference in the location of  $\text{NO}_2$  groups gives the three forms different dipole moments. The

largest dipole moment is 6.12 D for PNA, while ONA exhibits the smallest dipole moment: 4.26 D ( $D = 3.3356 \times 10^{-30}$  Cm). Therefore, one would expect the pyroelectric coefficient of TGS crystals doped with PNA to be higher than that for samples doped with ONA. This was the observation of Krajewski and Breczewski (1980) for a dopant concentration of about 3000 ppm which is about 15 times that of the present study. So, it seems that the low concentration of the dopant molecules in our case, and hence the internal bias, is not sufficient to convert the entire crystal into a single-domain one. This was confirmed by a difference observed between the results before and after the poling process. Accordingly, the pyroelectric coefficient of the ONA-doped crystal may be higher than that of the PNA-doped TGS crystals depending on domain configuration in the two cases.

Aniline is an organic compound that has in its structure the  $\text{NH}_2$  groups which appear in TGS. The permanent dipole moment of the aniline molecule is small; 1.53 D, compared with that of the nitroaniline group. Eisner (1978) reported an increase of about three times in the pyroelectric hysteresis loop after doping TGS crystals with 0.5% aniline. The high increase in the pyroelectric signal of aniline-doped TGS crystals seems to be in accordance with our results. The results of Eisner (1978) may also be considered as a confirmation of our assumption on the relation between the dipole moment of the dopant molecule and its effect on the pyroelectric coefficient of the matrix crystal.

The considerable pyroelectric signal which is still detected for the doped samples in a temperature range above  $T_c$  for pure samples is an interesting result. This temperature range reaches about 10 K for the d-l-alanine-doped sample while it is only about 4 K for the PNA-doped sample. The existence of this temperature range means a broadened transition from the polar to the non-polar phase. This broadened transition is a direct consequence of the electric bias created by the dopant and which still effectively acts in this temperature range. According to Martinez *et al* (1983) the bias field associated with l-alanine in TGS crystals decreased by more than two orders of magnitude within 1 K before  $T_c$ . If we correlate our results with the result of Martinez *et al* (1983) it would seem reasonable to assume that the bias fields in different samples decay in the vicinity of the phase transition in different ways depending on the difference in physical and chemical character of the dopant molecule. A preliminary experiment to study the temperature dependence of the bias field in TGS crystals doped with different organic molecules confirmed this assumption. However, this work is still being developed in our laboratory.

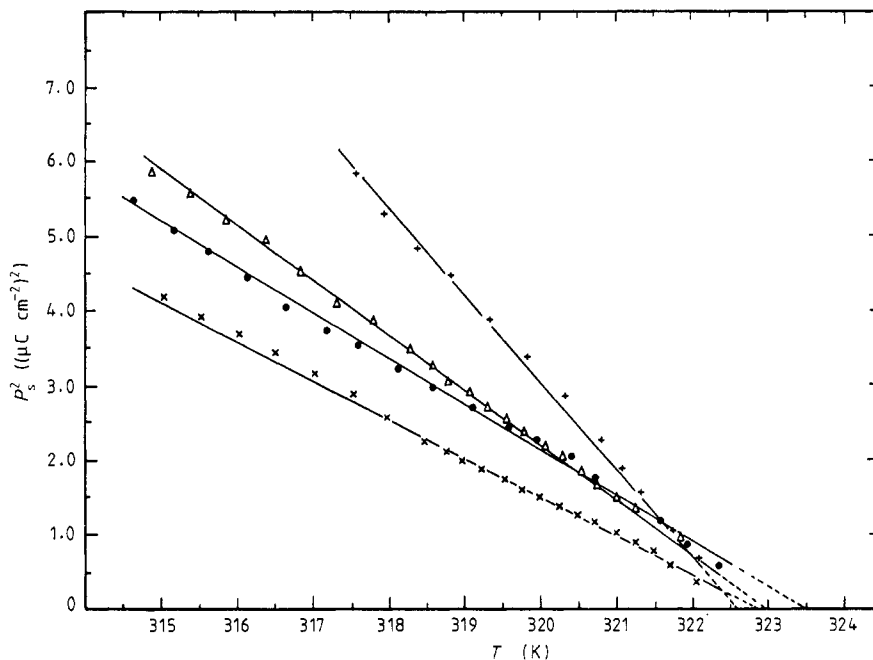
The value of the internal bias may be estimated from the peak value,  $p_{\max}$ , of the pyroelectric coefficient using the following equation (Pykacz 1978)

$$E_b = \alpha^3 / 27 \xi^2 p_{\max}^3$$

where  $\frac{1}{2}\alpha(T - T_0)$  and  $\xi/4$  are the coefficients of the terms  $P^2$  and  $P^4$  in the free-energy expansion under an external field and  $P$  is the polarisation. The values of  $\alpha$  and  $\xi$  were computed for the crystals used in the present investigation (Gaffer *et al* 1989) and hence the internal bias could be estimated. The result of such calculations gives 5.6, 25.5, 8.9 and 66  $\text{kV m}^{-1}$  for d-l-alanine-, ONA-, PNA- and aniline-doped samples respectively. These values seem to be in accordance with the values reported by Keve (1975) and Martinez *et al* (1983) for TGS crystals doped with l-alanine after taking in consideration the difference between the dopant content in the respective cases.

### 3.2. Spontaneous polarisation

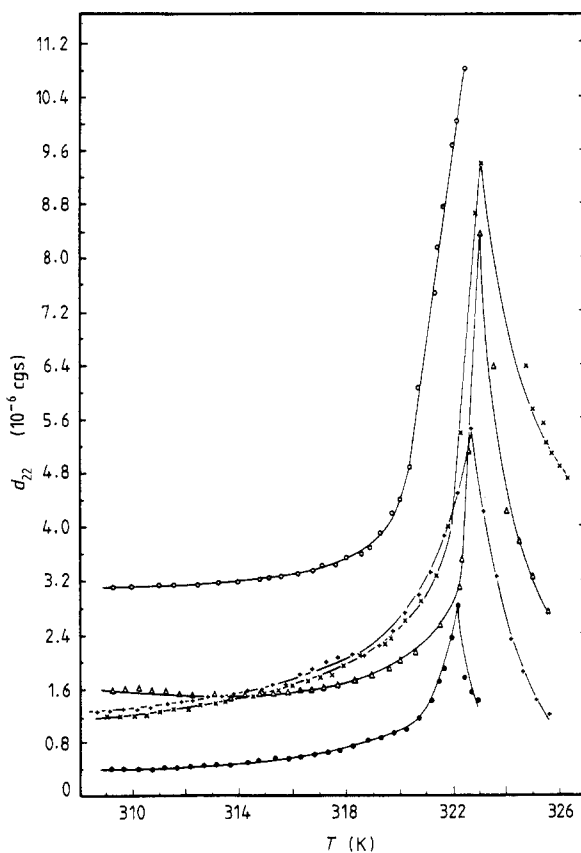
Spontaneous polarisation,  $P_s$ , of the studied crystals can be investigated through their pyroelectric properties since  $p = \partial P_s / \partial T$ . The temperature dependence of  $P_s$  for the



**Figure 3.** The temperature dependence of  $P_s^2$  of TGS crystals doped with organic molecules. ●, d-l-alanine-doped TGS; △, ONA-doped TGS; ×, PNA-doped TGS; +, aniline-doped TGS.

doped samples as well as the pure one is shown in figure 2. The spontaneous polarisation of doped samples increased in the same sequence of dopants as the pyroelectric coefficient. Comparing the  $P_s$  data for the crystals investigated in the present study and those of Keve (1975) for pure TGS indicates that  $P_s$  no longer goes directly to zero at the Curie temperature of pure TGS. The  $P_s$ - $T$  dependence inflected at some point and hence  $P_s$  continues to decrease with another decreasing rate. The critical behaviour at the transition becomes less pronounced and the transition from the ferro- to the paraelectric phase occurs in a wider temperature range. This broadened transition leaves the doped crystals polarised in a limited temperature range above  $T_c$  for pure TGS crystals. This characteristic has advantages for the application of TGS to IR detectors (Keve 1975).

Excluding the results of  $P_s$  after the 'inflection point' near  $T_c$  of pure crystals, the relation between  $P_s^2$  and  $T$  is a straight line (figure 3). From the straight-line behaviour the Curie temperature and the second coefficient,  $\xi$ , in the free energy expansion in powers of  $P_s$  could be calculated. The values of  $\xi$  given from this calculation are  $7.68 \times 10^{-10}$ ,  $7.29 \times 10^{-10}$ ,  $9.99 \times 10^{-10}$  and  $5.22 \times 10^{-10}$  esu in the case of d-l-alanine-, ONA-, PNA- and aniline-doped samples respectively. Comparing these values with the value of  $\xi$  for pure TGS crystals,  $8.97 \times 10^{-10}$  esu, it is obvious that aniline molecules have the strongest effect on the second coefficient of the free-energy expansion in powers of the polarisation which means that the spontaneous polarisation of the aniline-doped sample before the 'inflection point' decays faster to zero. Also, the values obtained for the Curie temperature,  $T_c$ , are 323.5, 323.0, 322.9 and 322.6 K for d-l-alanine-, ONA-, PNA- and aniline-doped crystals respectively. The effect of doping TGS with organic molecules on  $T_c$ , which is about 322.5 K for the pure sample, is clear.

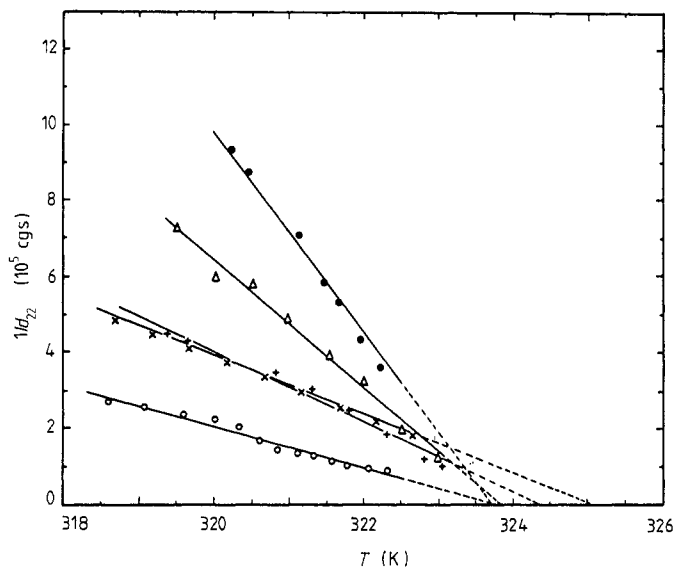


**Figure 4.** The temperature dependence of the piezoelectric modulus  $d_{22}$  of TGS crystals doped with organic molecules. The results for the pure sample are also presented.  $\circ$ , pure TGS;  $\bullet$ , d-l-alanine-doped TGS;  $\triangle$ , ONA-doped TGS;  $\times$ , PNA-doped TGS;  $+$ , aniline-doped TGS.

### 3.3. Piezoelectric modulus

A correlation between the structural changes at phase transition and the electrical behaviour may be obtained through study of the piezoelectricity of the crystal. Figure 4 shows the temperature dependence of the piezoelectric modulus in the direction of the polar axis,  $d_{22}$ , of the doped TGS samples. In the figure, results for pure TGS are also given. The frequencies at which the resonance and antiresonance occurred decreased with increasing temperature, a characteristic which is essentially related to the decrease in elasticity with temperature. The sharp rise in  $d_{22}$  for pure TGS close to the phase transition may be due to the increase in the mobility of domains on approaching the Curie point (Silvestrova and Yurin 1963). From the figure pronounced changes in the behaviour of  $d_{22}$  with temperature for TGS after doping are observed. The curves representing  $d_{22}$  for the doped samples are all depressed, the maximum depression appears for the d-l-alanine sample. This behaviour may be confirmed by our assumption that the presence of d-l-alanine tends to minimise the number of domains in the crystal. After reaching its maximum value  $d_{22}$  decreases steadily to zero. For several degrees of temperature in the paraelectric phase,  $d_{22}$  is still detected for the doped samples. This behaviour is quite different from that of the pure case. This behaviour may be attributed





**Figure 5.** The temperature dependence of the reciprocal of the piezoelectric modulus of TGS crystals, pure as well as doped with organic molecules. ○, pure TGS; ●, d-l-alanine-doped TGS; △, ONA-doped TGS; ×, PNA-doped TGS; +, aniline-doped TGS.

to the distorted areas formed by the dopant molecules within the matrix. The effect of these areas becomes relatively stronger in the region of the phase transition where the effects of the original matrix decay while approaching  $T_c$ . The steady decay of  $d_{22}$  for the doped samples in the non-polar phase is a direct consequence of the decay of its internal bias field.

In a limited temperature range, before its maximum value,  $d_{22}$  may be represented by a relationship of the form (figure 5)

$$d_{22} = D/(T_0 - T) \quad T_0 > T$$

where  $D$  is a constant and  $T_0$  is a temperature which slightly differs, for the doped samples, from the Curie point  $T_c$  of pure TGS. The values of  $D$  are  $1.83 \times 10^{-6}$ ,  $4.19 \times 10^{-6}$ ,  $5.84 \times 10^{-6}$ ,  $13.03 \times 10^{-6}$  and  $10.67 \times 10^{-6}$  cgs  $K^{-1}$  while the corresponding values of  $T_0$  are 323.7, 323.9, 322.8, 325.1 and 324.3 K for pure, d-l-alanine, ONA-, PNA- and aniline-doped samples respectively. A similar relationship for the piezoelectric stress constant  $e_{23}$  of TGS crystals in a temperature range far from the transition point was found by Baják (1975).

#### 4. Conclusions

Triglycine sulphate single crystals grown in the presence of 2 weight% of d-l-alanine, ONA, PNA or aniline molecules are characterised by a steady internal bias field which is responsible for the behaviour in the vicinity of the phase transition. The low concentration of the dopant molecules is probably not enough to create a sufficient bias to convert the crystal to a single-domain one. The pyroelectric coefficient was observed to increase and the temperature of the peak value was shifted after doping the TGS crystals.

The value of the internal bias may be estimated using the peak value of the pyroelectric coefficient. The bias field decays in the vicinity of the phase transition. The broadened transition from the ferro- to the paraelectric phase, the significant pyroelectric signal detected in the non-polar phase and the depression and systematic decay of the piezoelectric modulus before its disappearance are all direct consequences of the internal bias created by the dopants and its temperature dependence in the vicinity of the phase transition.

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