DIELECTRIC RELAXATION PROCESS IN DIGLYCINE NITRATE (DGN)

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The dielectric permittivity and dielectric losses of diglycine nitrate along the ferro-electric (101) direction have been measured at 80, 603, 1845 and 9450 MHz as a function of temperature. Dielectric relaxation was observed both in the paraelectric and ferroelectric regions. The relaxation was of the Debye type with a single relaxation time even in the immediate vicinity of the Curie point. It was found that distributions of the relaxation times in the vicinity of the Curie point are observed only in some crystals with a certain amount of dislocations and other imperfections.

1. Introduction

A number of studies on the dielectric relaxation in ferroelectric crystals have been reported, but only a part of them prove to be correct. Early results for Rochelle Salt [1] and TGS and deuterated TGS [2, 3] show the polydispersive nature of the dielectric relaxation process. It was suggested that in both substances a dispersion of the dielectric relaxation time may be described by a Gaussian distribution. Similar behaviour of the dielectric response was postulated in KNO_3 [4], $Ca_2Sr(C_2H_5CO_2)_6$[5], and Diglycine Nitrate DGN [6]. In all these substances the occurrence of the dielectric dispersion with many relaxation times was reported.

On the other hand Sandy and Jones [7], Kołodziej [8], Luther and Müser [9] reexamined RS and TGS, showing in all cases the simple monodispersive nature of the relaxation process. Similarly, the same nature of relaxation in thiourea [10], MASD [11], MCrSD [12], and $NaNO_2$ [13] was observed. The paraelectric phases of these crystals show a distribution of the dielectric relaxation time in the immediate vicinity of the Curie point, only, with β-factor of 0.90–0.94. It seems that this behaviour is presumably typical for all ferroelectrics of the order-disorder type. However, some results obtained by Unruh and Wahl [14] for TGS show that even in the immediate vicinity of the Curie point $49.15 \pm 0.1°C$

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the character of the dielectric relaxation is monodispersive. On the basis of the above results Unruh and Wahl suggested that distributions of the relaxation times observed in several ferroelectric crystals in the immediate vicinity of the Curie point are due to the imperfection of the domain structure.

The aim of the present work was to reexamine the dielectric relaxation in diglycine--nitrate DGN, particularly in the vicinity of the Curie point. Secondly, it was to check the extent to which the "critical retardation" process is responsible for the dielectric relaxation in this crystal.

2. Experimental

Diglycine-nitrate was obtained by slow evaporation of the aqueous solution which contained stechiometric quantities of glycine and nitric acide. By proper control of temperature and evaporation intensity of the solvent one obtains optically uniform crystals.

A crystal was cut to the desired shape and polished to the required dimension of $3 \times 3 \times 1.2$ mm. After polishing the sample, electrodes of conducting silver paint were applied to the polished parallel surfaces, which where perpendicular to the (101) direction.

Measurement method

The measurement method used in this work is slightly modified in comparison to that described previously [15, 16]. When the frequency becomes larger than 1 GHz the effect can be seen which is connected with the higher-order patterns of microwave. This gives rise to non-uniform field effects and makes the measurement particularly sensitive
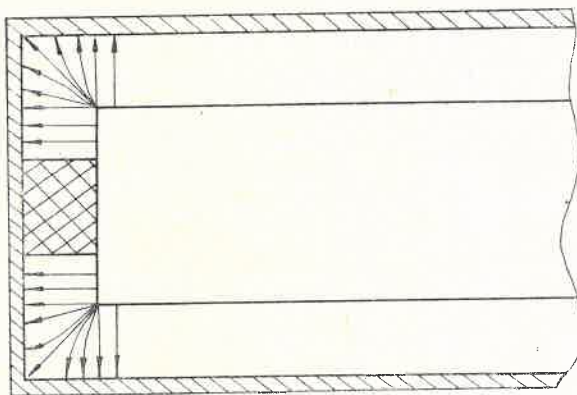

Fig. 1. Sample holder with the distribution of the electric field

to the shape and orientation of the sample. Kołodziej [17] has proposed a so-called "calibration" method which is based on the properties of a microwave four-terminal network [18, 19]. For this particular use we have to assume that higher order modes generated near the corner (see Fig. 1) have been attenuated before reaching the sample. It can be handled

if $r_2 \gg r_1$. This allows one to establish a reference plane l_2 on equivalent circuit at the sample-air interface as shown in Fig. 2. The voltage and current at l_1 and l_2 can be written as [19]

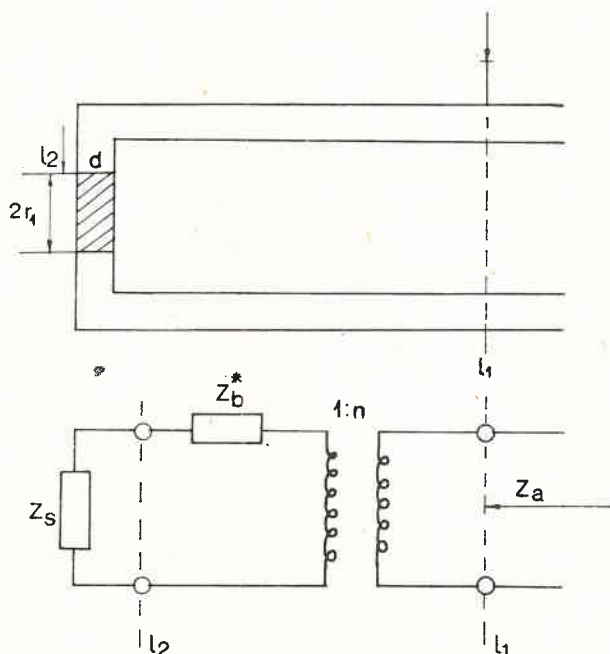$$U_1 = b_{11}U_2 + b_{12}I_2, \quad I_1 = b_{21}U_2 + b_{22}I_2. \tag{1}$$

Fig. 2. The equivalent circuit for the system shown in Fig. 1

Then

$$Z_a = \frac{b_{11}U_1 + b_{12}I_2}{b_{21}U_2 + b_{22}I_2} = \frac{b_{11}Z_s + b_{12}}{b_{21}Z_s + b_{22}} = \frac{1}{i\omega C_d^*}, \tag{2}$$

where C_d^* is the dynamic complex capacitance measured on the slotted line.

From the microwave circuit theory for this particular case [20]

$$b_{11}b_{22} - b_{12}b_{22} = 1; \quad b_{21} = ia_{21}. \tag{3}$$

Now, from equation (2) we can write

$$C_d^* = b_{12}^{-2}C_s^* + \frac{a_{21}}{b_{11}}, \tag{4}$$

and

$$C_s^* = b_{11}^2 C_d - \frac{a_{21}b_{11}}{\omega} = n^2 C_d^* - C_b, \tag{5}$$

where C_s is the static capacitance of the sample, $Z_s = \dfrac{1}{i\omega C_s}$, C_b is the total additional capacitance of the system, and $Z' = \dfrac{1}{i\omega C_b}$.

After separation of the real and imaginary parts of equation (5), one obtains

$$C'_s = tC'_d - C_b, \tag{6}$$

$$C''_s = tC''_d, \tag{7}$$

where $t = n^2$ is the transformer coefficient; the values of t and C_b depend on ω and r_1, and must be obtained for each frequency and dimension of the sample, e. g. by measurements of two samples with known ε^* (standard specimens such as TiO_2, $NaCl$, $CaSO_4$). Hence the final equation for t and C_b are:

$$t = \frac{C'_{1s} - C'_{2s}}{C'_{1d} - C'_{2d}}, \tag{8}$$

$$C_b = \frac{C'_{2d} C'_{1s} - C'_{2s} C'_{1d}}{C'_{1d} - C'_{2d}}. \tag{9}$$

The reference plane I_1 is obtained during the measurement of the equivalent metallic sample. All dimensions must be the same for the metallic, the standard, and the unknown sample. This method can be applied up to 18 GHz but, when $v \geqslant 10$ GHz, the phase shift $\varDelta$ between the metallic and dielectric samples becomes very small and sometimes to measure. In this case a special tapered or step-microwave transformer should be used with the transformation coefficient, t between 10 and 20, which permits one to measure $\varDelta$ of less than 0.1, 0.1 mm with a precision of $\pm 10\%$. The method described here permits measurement of the electric permittivity ε' with acceptable significance $\pm 10\%$ up to 5 GHz, from 5 to 10 GHz to about $\pm 15\%$, and from 10–18 GHz to $\pm 20\%$; also ε'' up to 5 GHz at $\pm 15\%$, from 5 to 10 GHz at $\pm 20\%$ and from 10 to 18 GHz at $\pm 30\%$. This is still reasonable precision compared with other methods.

Measuring procedure

A diagrammatic representation of the apparatus which was used from 80 MHz to 18 GHz is shown in Fig. 3.

The measurement procedure, which is common to all frequency range, is as follows: (*i*) The metallic sample is clamped in the sample holder. The standing mode position should be found; this is equivalent to the reference plane l_1; (*ii*) The metallic sample is replaced by two standard specimens, successively. The SWR (standing wave ratio) and $\varDelta$ (phase shift) relative to the reference plane l_1 are measured for both standard samples; (*iii*) The standard specimens are replaced by the unknown specimen and again the SWR and are relative to the reference plane l_1; (*iv*) The SWR and $\varDelta$ which have been obtained
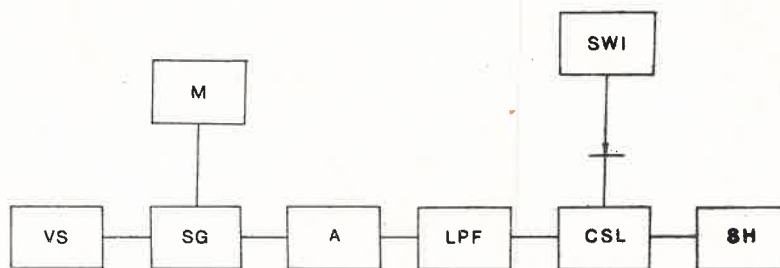
Fig. 3. Block diagram of the apparatus for complex electric permittivity measurement up to 18 GHz; VS — voltage supply; SG — signal generator; M — modulator; A — attenuator; LPF — low-pass filter; CSL — coaxial slatted line; SWI — standing wave indicator; SH — sample holder

for both standard specimens permit one to find the values for C'_{1d} and C'_{2d} by using the following equations [15]

$$C'_{1d} = \frac{(S^2-1)\tan\dfrac{2\pi\Delta}{\lambda}}{Z_0\omega\left(1+S^2\tan^2\dfrac{2\pi\Delta}{\lambda}\right)},$$

(10)

$$C''_{1d} = \frac{S\left(1+\tan^2\dfrac{2\pi\Delta}{\lambda}\right)}{Z_0\omega\left(1+S^2\tan^2\dfrac{2\pi\Delta}{\lambda}\right)},$$

(11)

where S is the SWR, and Z_0 is the standard characteristic impedance of the coaxial slotted line; (v) From the dimensions of the standard specimens, C'_{1s} and C'_{2s} can be obtained; (vi) By using equations (8) and (9) one can now very easily calculate "t" and C_b; (vii) By using values from (v) and (vi) and applying equations (10), (11), (6) and (7) C'_s and C''_s may be obtained; (viii) Finally, one can calculate the values for ε' and ε'' by using the following equation:

$$C_1 = \frac{1}{1.8k^2 d}\frac{k\sqrt{\overline{\varepsilon^*}}\,r_1 k\sqrt{\overline{\varepsilon^*}}\,r_1}{J_0 k\sqrt{\overline{\varepsilon^*}}\,r_1}\ [pF]$$

(12)

where J_0 is a zero-order Bessel function, J_1 is a first-order Bessel function.

3. Results and discussion

Table I shows the results of the measurements of ε' and ε'' as a function of frequency and temperature.

The phase transition temperature which was observed in the present work ($-67°C$) is in good agreement with the T_C reported in Ref. [21], ($-67°C$).

TÁBLE I

$(T-T_\theta)$			Para							Ferro						
			0.5	1.0	1.5	2.0	3.0	4.0	5.0	−0.5	−1.0	−1.5	−2.0	−3.0	−4.0	−5.0
1. Fre-quency MHz	80		440	340	270	233	184	150	125	460	360	240	155	114	80	58
			230	115	60	40	24	15	10	290	105	54	28	18	11	8
	603		170	182	183	178	163	147	125	150	144	135	126	104	77	54
			292	210	145	118	81	61	41	300	195	135	84	40	22	10
	1845		43	48	55	61	73	77	76	42	44	51	58	57	49	49
			120	116	110	102	85	70	58	122	111	97	80	50	26	18
	9450		16.2	16.2	16.2	16.9	17.6	17.6	18.9	16.2	16.2	16.2	16.2	17.6	17.6	16
			26	26	26	26	25	24	24	26	25	25	25	24	24	23
2. $\tau \cdot 10^{10}$ s			4.92	2.86	2.13	1.74	1.33	1.13	0.91	5.06	3.70	2.67	1.94	1.14	0.82	0.69
3. ε_0			578	389	295	248	196	162	131	654	403	269	187	119	84	57
4. $\Delta F^* \dfrac{kcal}{mol}$			4.08	4.18	4.27	4.34	4.45	4.56	4.58							

Fig. 4 and 5 show ε' against T and ε'' against T respectively. It can be seen that the maxima of the ε' shift to a higher temperature with increasing frequency confirming the "critical retardation process" analysed by a number of authors [22—26]. From the representation of the relaxation in forms of the Cole-Cole relation

$$\varepsilon^* - \varepsilon_\infty = \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (i\omega\tau)^\beta}.$$

The Cole-Cole diagrams with the temperature as a parameter are shown in Fig. 6 and 7 in the ferro and paraelectric phases respectively. The results which were obtained in this work once more confirm the monodispersive nature of the dielectric relaxation in ferroelectric crystals of the order-disorder type $(\beta = 0.96$–$0.98)$ [23, 27—30]. However, some other kinds of ferroelectrics, such as KD_2PO_4 [31] and KNO_3 [4] show a distribution of relaxation time, but these results seems to be uncertain and measurements should be repeated. This conclusion can be made on the basis of several of our experiments with the samples of DGN with a certain amount of dislocations and other inhomogenities. In this case a pronounced distribution of the relaxation times even very far from the transition temperature is observed. It seems that such inhomogenities are merely responsible for a distribution of the macroscopic relaxation time, particularly in the immediate vicinity of the Curie point.

The dielectric relaxation time τ, defined by $\tau = 1/2\pi v_m$ where v_m is a frequency of which ε' is equal to $(\varepsilon_0 - \varepsilon_{00})/2$, is shown as a function of temperature in Fig. 8. The relaxa-
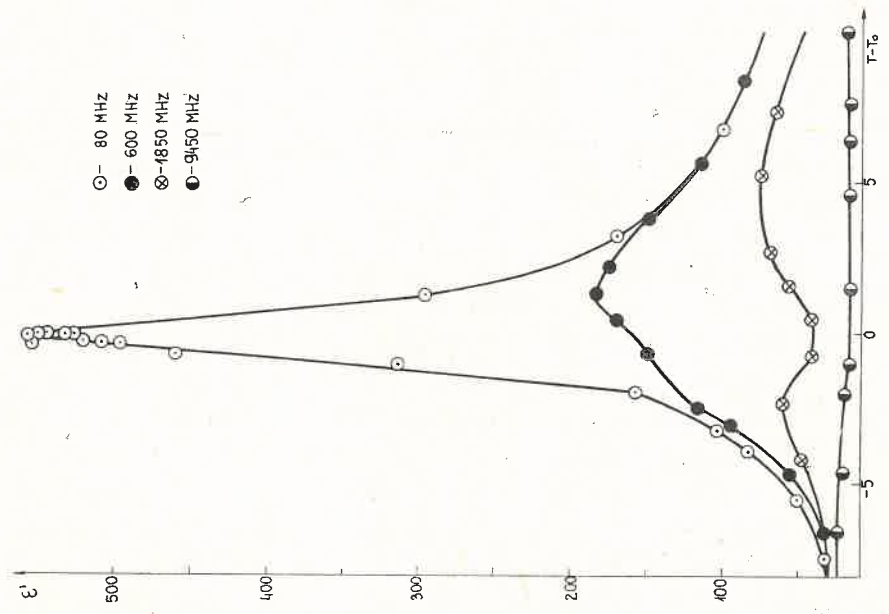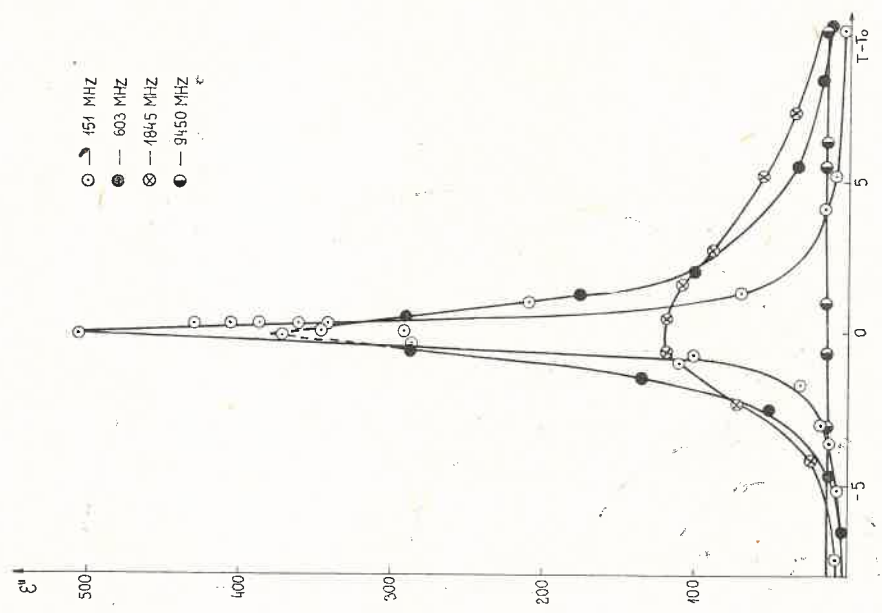
Fig. 4. The real part of the electric permittivity of DGN vs temperature at various frequencies

Fig. 5. The imaginary part of the electric permittivity of DGN vs temperature at various frequencies
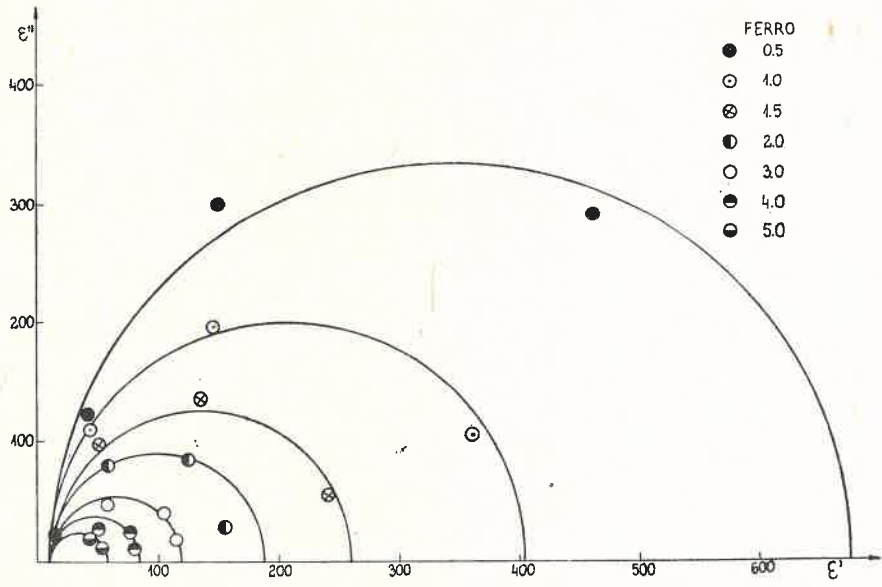
Fig. 6. The Cole-Cole diagrams with the temperature as a parameter in the ferroelectric phase
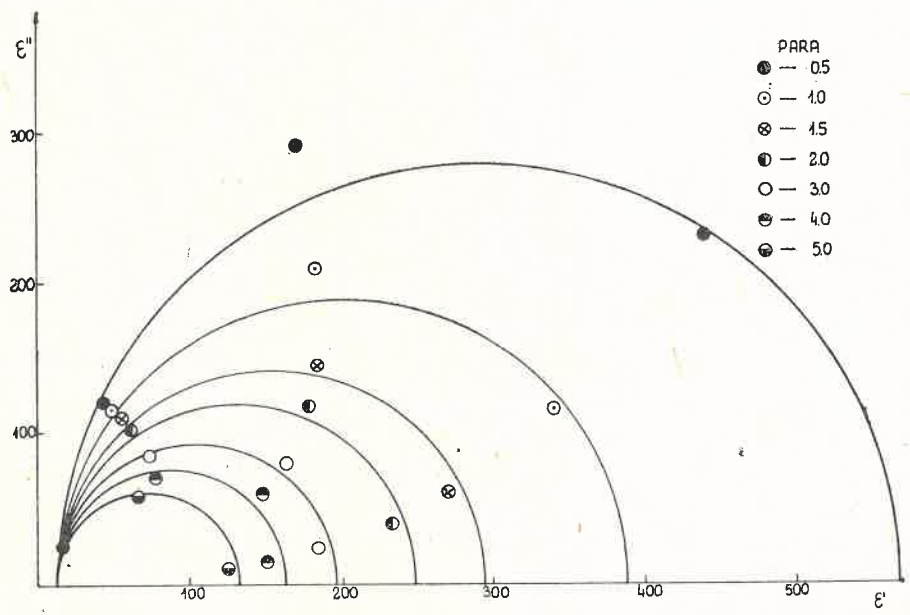

Fig. 7. The Cole-Cole diagrams with the temperature as a parameter in the paraelectric phase

tion time shows a sharp λ-type maximum of the Curie point showing a typical dielectric critical retardation. By using the above results and the following equation [29, 32]

$$\tau = \frac{h}{k(T - T_\theta)} \exp\left(\frac{\Delta F^*}{kT}\right) \tag{13}$$

the value of the activation energy for reorientation of a molecular dipole in the lattice may be obtained. The results are shown in Fig. 9. From these results it can be seen that in the paraelectric phase the activation energy decrease towards the transition point. This result
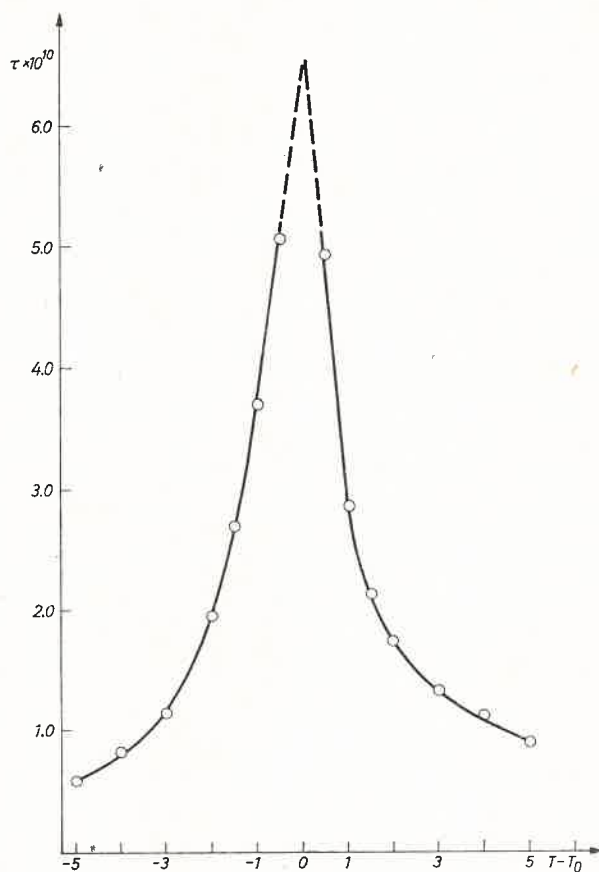

Fig. 8. The relaxation time vs temperature

for the slight increase of ΔF^* may be rather anomalous. It would in general be expected to decrease with increasing temperature due to the increase of the activation entropy term. However, the slight increase of ΔF^* with temperature may be explained as a result of thermal expansion. But in our case the above explanation cannot be accepted because of the large dependence of ΔF^* on temperature, particularly between 0 and 4 of $(T - T_\theta)$ value. At present, the physical meaning of the anomalous decrease of ΔF^* immediately

above the Curie point is not clear. However, one could say the relation (13) from which a value of ΔF^* has been obtained does not take into account any occurrence of a very strong fluctuation, particularly the local field fluctuation due to random jumping of a particle.
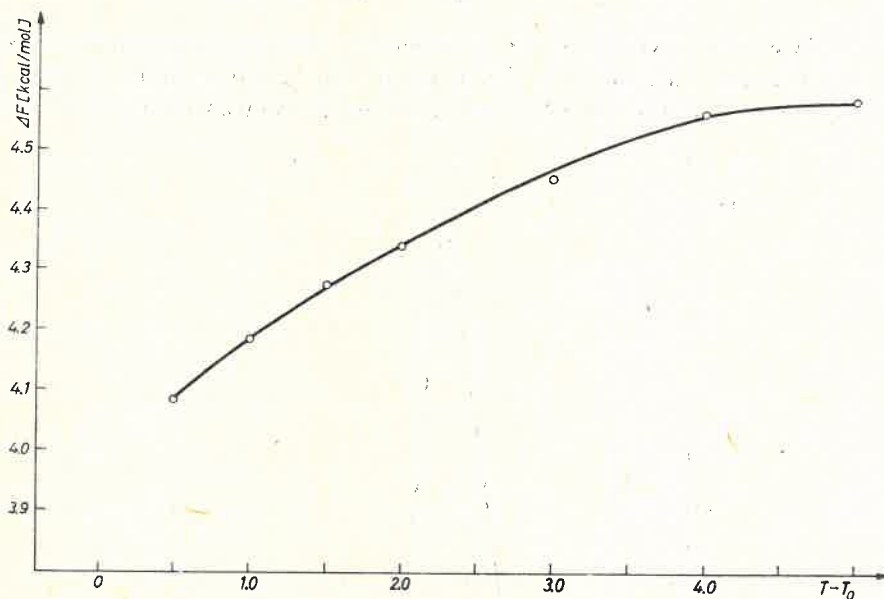

Fig. 9. The dependence of ΔF^* vs temperature

4. Conclusions

From the present study for DGN the following may be concluded:

1. The dielectric relaxation observed can be theoretically described to a good approximation by a monodispersive process in both para and ferroelectric phases;

2. The crystal shows the critical retardation process of the dielectric relaxation observed near the transition temperature.

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