

INFLUENCE OF ORTHO-NITROANILINE, META-NITROANILINE, PARA-NITROANILINE, AND L-ALANINE ADMIXTURES IN TGS CRYSTALS ON THE VELOCITY AND ABSORPTION OF QUASI-LONGITUDINAL ULTRASONIC WAVES*

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Applying the ultrasonic method, the velocity and absorption coefficient of a quasi-longitudinal ultrasonic wave of frequency 14.6 MHz propagating along the directions [100], [010] and [001] in TGS crystals, pure and admixed with the organic compounds ortho-, meta-, para-nitroaniline and L-alanine, are determined from 290 to 340 K. From the changes in absorption coefficient in the ferroelectric phase, the relaxation time of spontaneous polarization is determined and found to be enhanced by nitroaniline and lowered by L-alanine admixture. From the velocity dispersion, determined at the transition from para- to ferro-electric phase, the electrostrictive coupling coefficients q_{12} and q_{32} are calculated and found to be enhanced in the admixed crystals. Moreover, the admixed TGS crystals were found to exhibit an electric field, making the phase transition "diffluent".

1. Introduction

The phase transition of the second order occurring in ferroelectric triglycine sulphate (TGS) crystals has repeatedly been studied by ultrasonic methods applying frequencies of the 5 [1] to 125 [2] MHz range. However, in the majority of cases, the temperatures at which the absorption coefficients were measured was restricted to a range of two degrees centigrade about the Curie point [1-5]; nor were the velocity and absorption coefficient determined for the three principal crystallographical directions simultaneously, and no indication was given as to the single- or multi-domain nature of the samples.

Admixtures affect the propagation parameters of acoustic waves by causing modifica-

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tions in the dislocation structure of the crystal leading to scattering on perturbed regions and variations in the relaxation times of thermal phonons. Albeit, admixturing of ferroelectric crystals affects their physical properties the most strongly in the immediate neighbourhood of the phase transition. Hitherto, regrettably, there is a lack of reports concerning the influence of admixturing on the velocity and absorption of acoustic wave propagating in TGS crystals.

The aim of the present work was to determine the velocity and absorption coefficient for a quasi-longitudinal ultrasonic wave propagating in the three principal crystallographical directions of TGS crystals at temperatures in the range from 290 to 340 K, as well as the changes caused in these propagation parameters by the introduction, into the crystal lattice of TGS, of the foreign molecules: ortho-nitroaniline, meta-nitroaniline, para-nitroaniline, and L-alanine, with especial attention given to the neighbourhood of the Curie point, with the purpose hence to determine the changes in characteristics of the phase transition caused by the introduction of admixtures.

2. Preparation of the samples for investigation

Single crystals of triglycine sulphate, $(\text{NH}_2\text{CH}_2\text{COOH})_3 \cdot \text{H}_2\text{SO}_4$, for investigation were obtained by the isothermal method from an aqueous solution of the fivefold recrystallized salt. The crystals, both pure and admixtured, were grown at 316 K. Admixtured crystals were obtained from solutions containing ortho-, meta-, and para-nitroaniline, $\text{C}_6\text{H}_4\text{NO}_2 \cdot \text{NH}_2$, at a concentration of 0.25 % weight, and L-alanine, $\text{CH}_3\text{CHCOOH} \cdot \text{NH}_2$, at 3 % weight.

The concentration of the nitroaniline admixture to the crystal was determined spectrophotometrically applying extraction with ethyl ether. That of L-alanine was determined by paper chromatography. The admixture concentrations are given in Table I.

TABLE I

Admixture concentrations in the TGS crystals studied

Admixture	Concentration in the solution [% weight]	Concentration in the crystal [% weight]
ortho-nitroaniline	0.25	$1.5 \cdot 10^{-4}$
meta-nitroaniline	0.25	$4.2 \cdot 10^{-4}$
para-nitroaniline	0.25	$2.0 \cdot 10^{-4}$
L-alanine	3.0	$2.0 \cdot 10^{-2}$

The parameters of propagation of the acoustic wave i.e. its velocity and attenuation coefficient were determined by the ultrasonic pulse echo method. A piezoelectric transducer, 6 mm in diameter, made of barium titanate ceramics, generated a longitudinal

acoustic wave of frequency 14.6 MHz and pulse duration 1 μ s. Acoustic contact between the transducer and the crystal specimen was ensured by means of a thin layer of silicon oil — a material the acoustic properties of which remain constant throughout a wide range of temperatures [6, 7]. To reduce error, the thickness of the contact layer was kept constant in all the measurements by means of a spring clamp acting on the transducer and specimen.

Subsequent to growth, cubic samples were cut with edges of 1 cm and 1.5 cm from the TGS crystals in order to determine for each sample the velocity and attenuation coefficient in the crystallographical directions [100], [010] and [001]. The edges were oriented with an accuracy of $\pm 1^\circ$ with respect to the system of crystallographic axes proposed by Konstantinova et al. [8]. This degree of accuracy admits of an error of as little as 0.02% in determinations of the velocity [9]. The surfaces of the samples were ground and polished until a parallelity better than $2 \cdot 10^{-4}$ rad was achieved. The effect of this divergence on the attenuation coefficient amounted to 0.02 dB/cm [10,11] and lay well below experimental error. This degree of accuracy of sample preparation ensured the obtaining of a correct exponential decrease of the signal amplitudes of the echos.

A single-domain state of the crystals was achieved by way of their permanent polarization in an electric field of 100 kV/m subsequent to annealing or 10 — 20 hrs at 340 K. In order to avoid their depolarization between successive measurements, the crystals were re-immersed in the 100 kV/m field. Ultrasonic propagation measurements were performed in the temperature range from 290 to 340 K. The temperature was measured by the compensation method applying a copper-constantan thermocouple. The temperature of the samples was stabilized to within ± 0.01 deg.

3. Results of velocity measurements

The velocity of the acoustic wave determined by direct readings of the twofold traversal time of the pulse through the sample from the oscilloscope screen. To enhance the accuracy, the signals from a calibrated time marker were observed simultaneously. The accuracy thus achieved amounted to $5 \cdot 10^{-4}$.

The velocity values obtained for a quasi-longitudinal ultrasonic wave propagating in the three principal crystallographical directions of pure TGS crystal are given in Fig. 1, whereas Figs 2 — 5 show the temperature-dependent variations of the velocity in TGS crystals admixed with ortho-, meta- and para-nitroaniline as well as L-alanine. In all admixed TGS crystals in all three directions the velocity was found to undergo a slight enhancement due to scattering of the wave on distorted regions of the crystal lattice surrounding the molecules of the admixture [12].

In Table II, we give the values of the jumpwise change in velocity at the para- to ferro-electric phase transition, for pure and admixed TGS and the directions [001] and [100]. This parameter, which characterizes dispersion of velocity, is related with a relaxation process typical for phase transitions of the second order [13]. No relaxation of the ordering parameter occurs for wave propagation in the direction of the ferroelectric axis owing to long-range dipole-dipole interaction [14], and the velocity does not vary discontinuously in the Curie point [15].

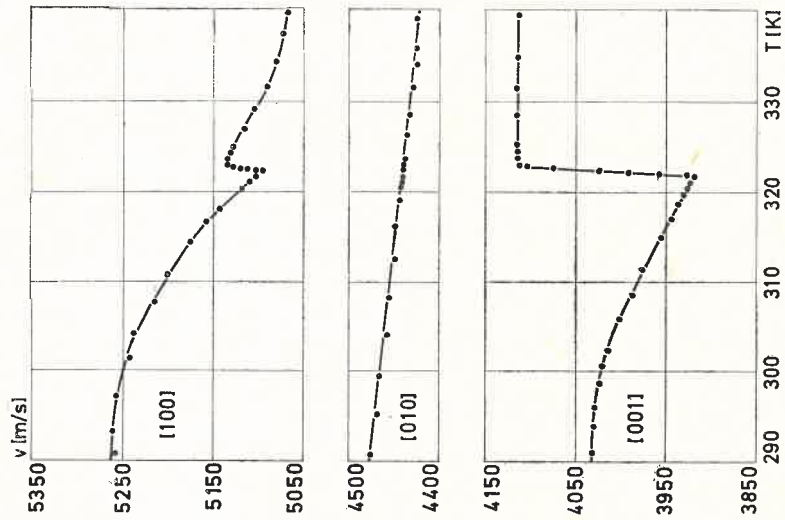


Fig. 1

Fig. 1. Velocity of quasi-longitudinal ultrasonic wave in pure TGS single crystal, for the three principal crystallographical directions
 Fig. 2. Velocity of quasi-longitudinal ultrasonic wave in ortho-nitroaniline admixed TGS single crystal, for the three principal crystallographical directions. Dashed line — wave velocity in pure TGS single crystal

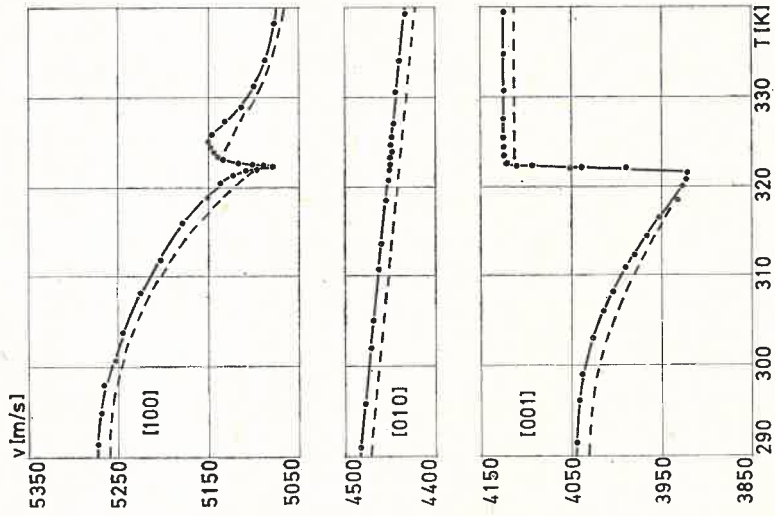


Fig. 2

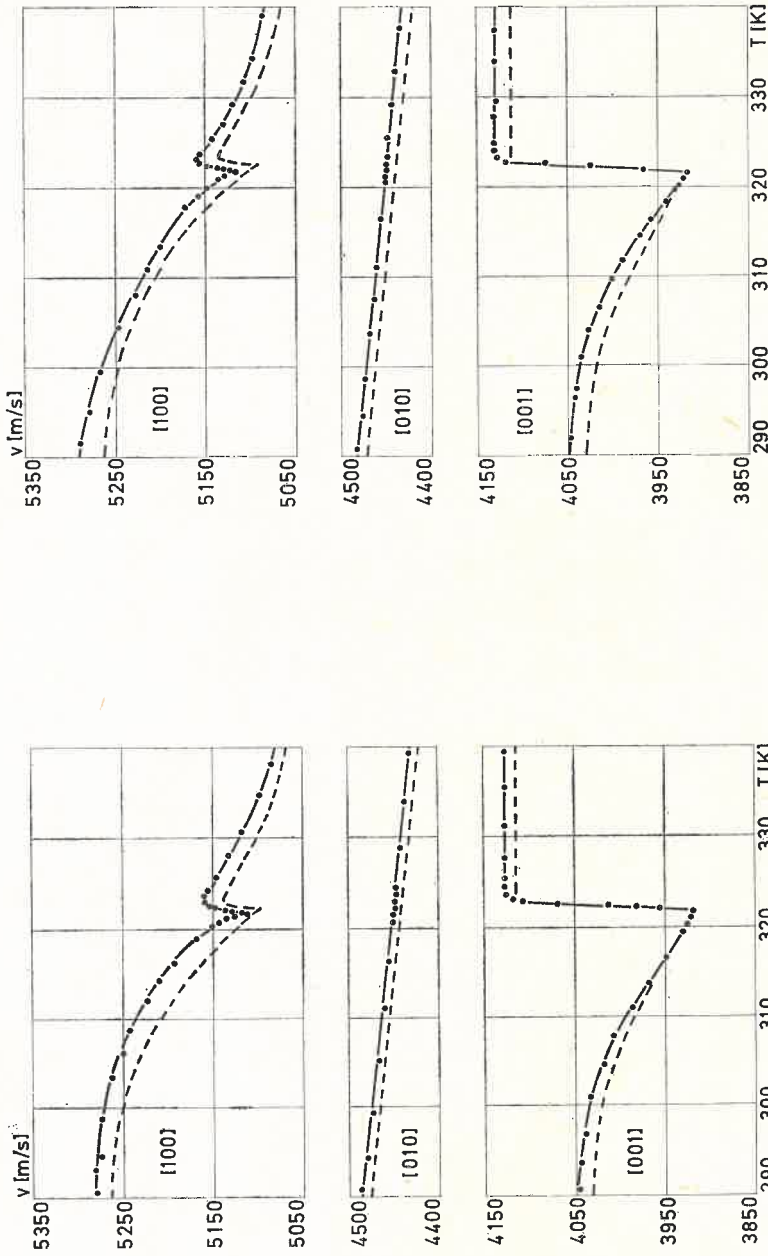


Fig. 3

Fig. 4

Fig. 3. Velocity of quasi-longitudinal ultrasonic wave in meta-nitroaniline admixed TGS single crystal, for the three principal crystallographical directions. Dashed line — wave velocity in pure TGS crystal

Fig. 4. Velocity of quasi-longitudinal ultrasonic wave in para-nitroaniline admixed TGS single crystal, for the three principal crystallographical directions. Dashed line — wave velocity in pure TGS crystal

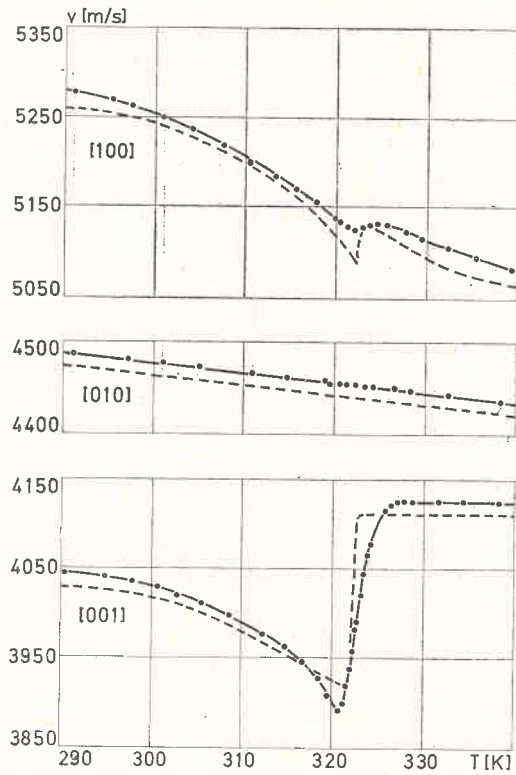


Fig. 5. Velocity of quasi-longitudinal ultrasonic wave in L-alanine admixed TGS single crystal, for the three principal crystallographical directions. Dashed line — wave velocity in pure TGS crystal

TABLE II

Dispersion of ultrasonic wave velocity

Crystal	$v_{\infty} - v_0$ [m/s]		$v_{\infty}^2 - v_0^2$ [m/s] ²	
	Direction		Direction	
	[001]	[100]	[001]	[100]
TGS pure	170	40	$1.36 \cdot 10^6$	$0.42 \cdot 10^6$
TGS admixed with ortho-nitroaniline	188	48	$1.50 \cdot 10^6$	$0.49 \cdot 10^6$
TGS admixed with meta-nitroaniline	220	45	$1.76 \cdot 10^6$	$0.46 \cdot 10^6$
TGS admixed with para-nitroaniline	180	73	$1.44 \cdot 10^6$	$0.74 \cdot 10^6$
TGS admixed with L-alanine	220	—	$1.76 \cdot 10^6$	—

4. Results of attenuation coefficient measurements

The attenuation coefficient of the ultrasonic pulse traversing the crystal sample was determined from the ratio of amplitudes of a series of echos, lying in the far diffraction zone. In order to obtain the attenuation due only to energy absorption in the material, we measured the attenuation coefficient for two samples of the same material 1 cm and

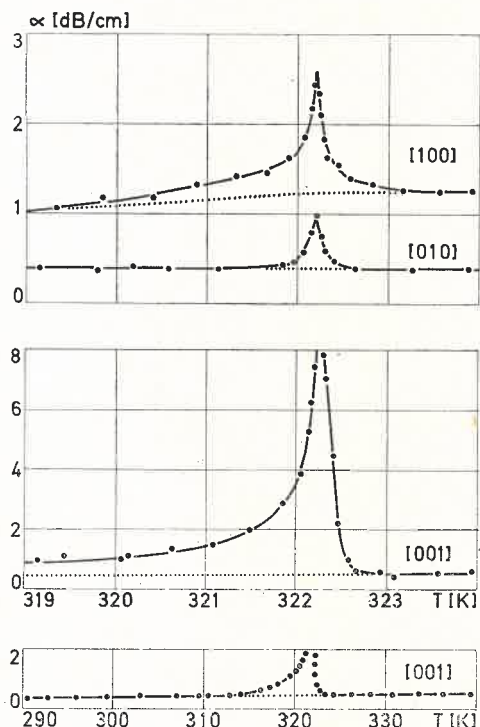


Fig. 6. Attenuation of quasi-longitudinal ultrasonic wave in pure TGS single crystal, for the three principal crystallographical directions. Dotted line—attenuation independent of relaxation and fluctuations of spontaneous polarization

1.5 cm thick. Losses by diffraction, determined after Refs [16, 17], amounted to 0.4 dB/cm for the piezoelectric transducer with 6 cm diameter applied in our measurements.

Fig. 6 shows the changes in attenuation coefficient for the quasi-longitudinal ultrasonic wave propagating in pure TGS crystal along the directions [100], [010] and [001] versus temperature, in the range from 290 to 340 K. Since the attenuation coefficient varies by a factor of 10—20 within a region of several degrees astride the phase transition temperature, the function $\alpha = \alpha(T)$ is plotted, for the sake of clarity, in two different temperature scales. Absorption of the wave is related with processes which, in the range studied, are temperature-independent, such as phonon-phonon interaction, dislocational friction and interaction between the wave and crystal lattice defects, as well as processes specific to ferroelectrics related with relaxation and fluctuation of the spontaneous polarization, which are strongly temperature-dependent in the region of several degrees to either side of the Curie point.

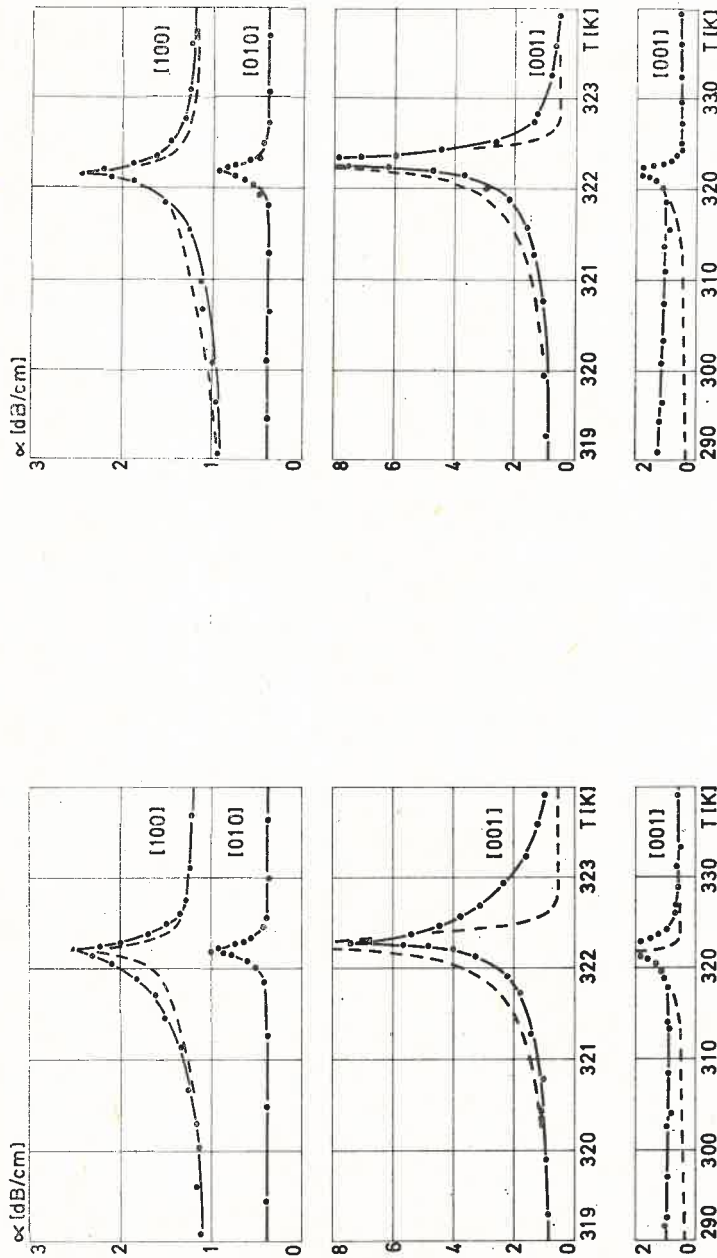


Fig. 7

Fig. 7. Attenuation of quasi-longitudinal ultrasonic wave in ortho-nitroaniline admixed TGS single crystal, for the three principal crystallographic directions. Dashed line — attenuation for pure TGS single crystal

Fig. 8. Attenuation of quasi-longitudinal ultrasonic wave in meta-nitroaniline admixed TGS single crystal, for the three principal crystallographic directions. Dashed line — attenuation for pure TGS single crystal

Fig. 8

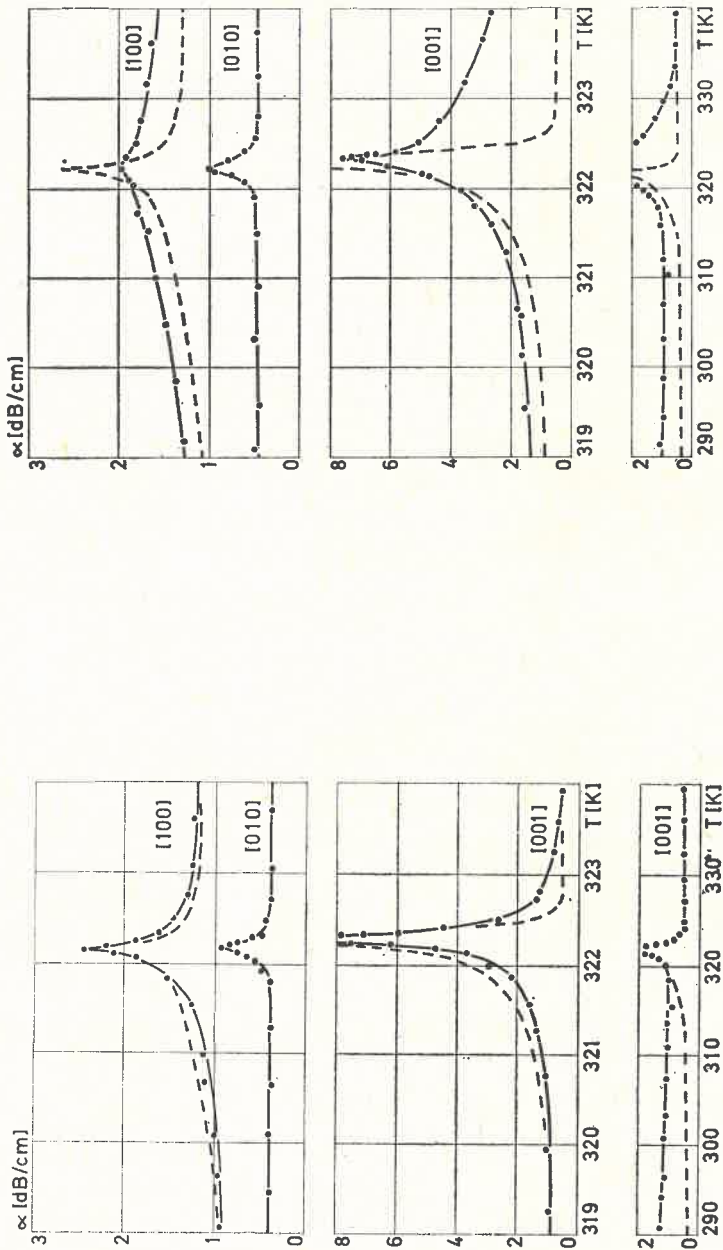


Fig 10

Fig. 9. Attenuation of quasi-longitudinal ultrasonic wave in para-nitroaniline admixed TGS single crystal, for the three principal crystallographic directions. Dashed line — attenuation for pure TGS single crystal

Fig. 10. Attenuation of quasi-longitudinal ultrasonic wave in L-alanine admixed TGS single crystal, for the three principal crystallographic directions. Dashed line — attenuation for pure TGS single crystal

The two groups of interaction are accessible to resolution by ultrasonic attenuation studies in a wide range of temperatures. In Fig. 6, the attenuation unrelated with processes specific to ferroelectrics is represented by a dotted line.

Figs 7 — 10 shows the attenuation coefficient versus temperature for the three principal directions of TGS crystals admixed with the compounds: ortho-nitroaniline, meta-nitroaniline, para-nitroaniline, and L-alanine. The dashed line indicates the values obtained in pure TGS monocrystal.

5. Determination of the relaxation time of spontaneous polarization

In accordance with the theory of Landau and Khalatnikov [13], describing the variations of the complex propagation vector k^* of an elastic wave in a medium characterized by a single relaxation time τ , the velocity and absorption coefficient are given, in the vicinity of a λ -type phase transition, by the following relations:

$$v^2 = v_\infty^2 - \frac{v_\infty^2 - v_0^2}{1 + \omega^2 \tau^2}, \quad (5.1)$$

$$\alpha = \frac{v_\infty^2 - v_0^2}{2v_\infty^3} \frac{\omega^2 \tau}{1 + \omega^2 \tau^2}, \quad (5.2)$$

with: v_∞ — the velocity of a wave with a frequency such that the stresses vary so rapidly that the ordering parameter cannot keep pace with them; and v_0 — the velocity of a wave with a frequency at which the vibrations occur sufficiently slowly for the system to be at equilibrium at each moment of time. The relaxation time of the ordering parameter, for a ferroelectric phase transition of the second order and a material not piezoelectric in the paraelectric phase, amounts to:

$$\tau = (2L\xi P_s^2)^{-1} \quad (5.3)$$

where L is the coefficient of the kinetic equation

$$\frac{\partial F}{\partial P_s} = - \frac{1}{L} \frac{dP_s}{dt} \quad (5.4)$$

and exhibits no anomaly at the phase transition temperature. Eqs (5.1) — (5.4) completely characterize the velocity and attenuation as functions of temperature in the vicinity of a phase transition of the λ -type.

The range of applicability of the Landau-Khalatnikov theory, which is based on the mean field approximation, is restricted by the condition $(T_c - T)/T_c > 10^{-4}$ [19] since in the immediate neighbourhood of the transition an important role is played by fluctuations of the ordering parameter not taken into consideration by the theory. Interaction of the acoustic wave and thermal fluctuations of the ordering parameter leads to an anomalous increase in absorption coefficient of the wave [15, 20]. The anomaly is symmetric with respect to the Curie point and independent of the propagation direction of the wave. Direction-dependent investigation of the propagation parameters of an ultrasonic wave propagating in uniaxial ferroelectrics, non-piezoelectric in the paraelectric phase, permits

the separation of the relaxational effect from the fluctuational effect, since in the case of propagation along the polar axis polarization relaxation vanishes owing to long-range dipole-dipole interaction [14, 15]. Consequently, investigation of attenuation of a longitudinal wave in the [010] direction enables one to determine the absorption related solely with thermal fluctuations of spontaneous polarization.

In the megahertz range of frequencies, $\omega\tau \ll 1$ and Eq. (5.2) reduces to

$$\alpha = A\omega^2\tau \quad (5.5)$$

where

$$A = \frac{v_\infty^2 - v_0^2}{2v_\infty^3}. \quad (5.6)$$

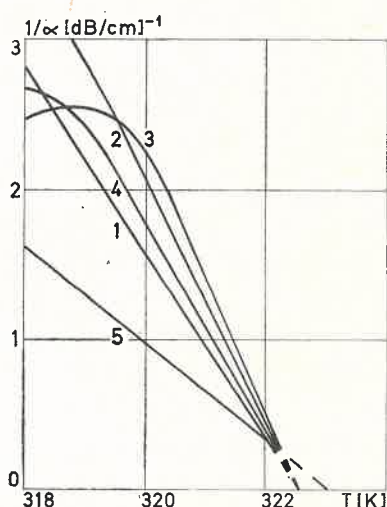


Fig. 11. Reciprocal value of relaxational attenuation in the admixed TGS crystals in the directions [001]: 1 — pure TGS; 2 — TGS admixed with ortho-nitroaniline; 3 — TGS admixed with meta-nitroaniline; 4 — TGS admixed with para-nitroaniline; 5 — TGS admixed with L-alanine

Experimental determination of $\omega^2/\alpha = (A/\tau)^{-1}$ for the direction [001] in pure TGS crystal led to

$$\omega^2/\alpha = 45.7 \cdot 10^{13} \cdot \Delta T.$$

Extrapolation of the straight line in Fig. 11 to the point of intersection with the axis of ordinates yielded for the phase transition temperature

$$T_c = 322.5 \text{ K.}$$

Having available the value of the jump in velocity at transition from the para- to the ferro-electric phase, we determined the coefficient A and hence the relaxation time of spontaneous polarization

$$\tau = \frac{2.4 \cdot 10^{-10}}{\Delta T} \text{ s.}$$

Having recourse to Eq. (5.3) and the values: $\xi = 72 \text{ cm}^4/\text{C}^2$ [21] and $P_s^2/\Delta T = 4.8 \cdot 10^{-5} \text{ C}^2/\text{m}^4\text{deg}$, we calculated the coefficient L of Landau's equation as:

$$L = 6.0 \cdot 10^{11} \text{ s}^{-1}.$$

In order to determine the effect of TGS doping on the relaxation time of spontaneous polarization, we plotted ω^2/α as a function of temperature for the directions [001] and [100] of the variously admixed crystals (Figs 11 and 12). The values obtained for the slope

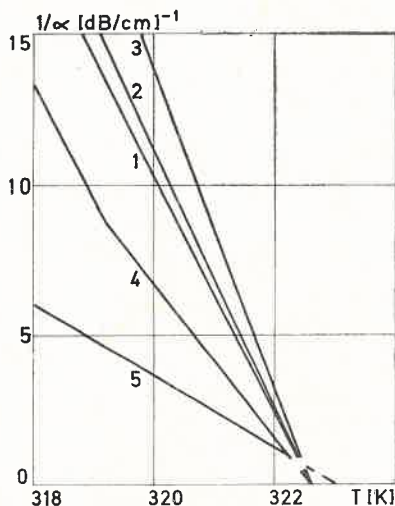


Fig. 12. Reciprocal value of relaxational attenuation in the admixed TGS crystals in the directions [100]: 1 — pure TGS; 2 — TGS admixed with ortho-nitroaniline; 3 — TGS admixed with meta-nitroaniline; 4 — TGS admixed with para-nitroaniline; 5 — TGS admixed with L-alanine

TABLE III

Slope of the function ω^2/α and relaxation time of spontaneous polarization for admixed TGS crystals

Crystal	Slope of $\omega^2/\alpha \cdot 10^{13} \cdot \Delta T$ [m/s ² deg]		Relaxation time $\tau \cdot 10^{-10}/\Delta T$ [s]	
	Direction		Direction	
	[001]	[100]	[001]	[100]
TGS pure	45.7	292	2.4	2.25
TGS admixed with ortho-nitroaniline	59.5	342	1.7	1.6
TGS admixed with meta-nitroaniline	67.0	400	1.3	1.4
TGS admixed with para-nitroaniline	49.7	190	2.1	1.9
TGS admixed with L-alanine	232	92	3.1	—

of the function ω^2/α are given in Table III. Next, on the basis of the velocity dispersion of Table II, we determined by Eqs (5.5) and (5.6) the polarization relaxation time for the directions [001] and [100] in TGS crystals admixed with the above stated organic compounds. The results are given in Table III.

The spontaneous polarization relaxation time, in pure and admixed TGS crystals, has the same value for both directions perpendicular to the ferroelectric axis. The increase in relaxation time (the time necessary for spontaneous polarization to attain equilibrium) due to an addition of L-alanine is indicative of a stiffening of the crystal lattice. A rigidification of the lattice of L-alanine doped TGS has also been observed in second dipole moment NMR measurements [22]. This corroborates the suggestion of Keve et al. [23] that the molecule of L-alanine is "built into" the crystal lattice of TGS partly replacing glycine I and that the perturbed region surrounding it is characterized by properties of the B-structure studied by Fletcher et al. [24]. Lock [25] as well as Bye and Keve [26] have established that the introduction of L-alanine into TGS causes an electric field to be induced in the crystal forcing it to assume a permanent single-domain state and making the phase transition "diffluent". Such crystals have also been found to exhibit a diffuence of the phase transition in measurements of ultrasonic wave velocity and attenuation.

6. Determination of electrostrictive coupling coefficients

By having recourse to the free energy expansion for ferroelectrics and the assumption that the ultrasonic wave causes small fluctuations of the spontaneous polarization about its equilibrium value, O'Brien and Litovitz [2] and Bajak [18] derived the following expression for the complex elasticity module

$$c_{ii}^* = c_{ii}^p - \frac{2q_{i2}^2/\xi}{1 + i\omega\tau} \quad (6.1)$$

where $\tau = (2L\xi P_2^2)^{-1}$; c_{ii}^p are the elasticity modules at constant polarization; and q_{i2} the electrostrictive coupling coefficients, relating the stress σ_i and polarization P_2 .

For high ultrasonic frequencies, when the changes in polarization fail to keep pace with the acoustic field $\omega\tau \gg 1$

$$c_{ii}^{(\infty)} = c_{ii}^p = \rho v_\infty^2. \quad (6.2)$$

On the other hand, at low frequencies $\omega\tau \ll 1$

$$c_{ii}^{(0)} = c_{ii}^p - 2q_{i2}^2/\xi = \rho v_0^2. \quad (6.3)$$

One hence determines the velocity dispersion for the wave as

$$v_\infty^2 - v_0^2 = 2q_{i2}^2/\xi\rho. \quad (6.4)$$

Thus, if the jumpwise change in velocity at transition from the para- to the ferro-electric phase is known, one is in a position to calculate the electrostrictive coupling coefficients

$$|q_{i2}| = \sqrt{1/2(v_\infty^2 - v_0^2)\xi\rho}. \quad (6.5)$$

TABLE IV

Values of electrostrictive coefficients for admixed TGS crystals

Crystal	Electrostrictive coefficients	
	q_{12}	q_{32}
TGS pure	1.7	3.3
TGS admixed with ortho-nitroaniline	1.85	3.45
TGS admixed with meta-nitroaniline	1.80	3.7
TGS admixed with para-nitroaniline	2.2	3.45
TGS admixed with L-alanine	—	3.7

The electrostrictive coefficients q_{12} and q_{32} thus determined for pure and admixed TGS crystals are given in Table IV.

All the compounds applied by us as admixtures to TGS cause an increase of the electrostrictive coupling coefficients.

7. The internal electric field existing in admixed TGS crystals

Isolated, electrically charged defects, when present in the crystal lattice, give rise to an electric field within the crystal [27]. The internal field thus produced strongly affects the temperature-dependence of the parameters defining the propagation of ultrasonic waves. The field can be assessed quantitatively by comparing the changes caused in some physical property of the crystal by a known, externally applied DC field and, on the other hand, by the introduction of an admixture. In the ferroelectric phase, an external field will polarize the crystal and lower the relaxation time of its spontaneous polarization, whereas in the paraelectric phase it contributes to induce polarization leading to an increase in absorption. As a result of the two processes, the sharp maximum of the absorption coefficient at the transition temperature undergoes a "flattening and diffuence" [28]. Also, the change in velocity at transition from the ferroelectric to the paraelectric phase occurs gradually rather than jumpwise [29].

The changes in acoustic wave velocity and attenuation due to the electric field of the admixtures are the most strongly apparent for propagation in the [001] direction in temperatures up to several degrees above the Curie point. By comparing the changes in propagation parameters for the admixed crystals and those caused in pure TGS crystals by an external field applied along the [010] direction we evaluated the strength of the internal electric field due to the admixtures in polarized TGS crystals. The values thus obtained are to be found in Table V.

In addition to causing a "diffuence" of the absorption anomaly, the electric field leads to a shift in Curie point towards higher temperatures. Whereas the TGS crystals doped with L-alanine exhibited a shift amounting to 0.4 deg, those containing nitroanilines

TABLE V

Internal electric field strengths in admixed TGS crystals

Crystal	Internal electric field strength E [kV/m]
TGS admixed with ortho-nitroaniline	ca 70
TGS admixed with meta-nitroaniline	25 ÷ 30
TGS admixed with para-nitroaniline	ca 20
TGS admixed with L-alanine	200 ÷ 250

failed to exhibit a measurable displacement of the Curie temperature because of the low values of the fields produced by the latter admixtures.

The pure TGS crystals too exhibited anomalous attenuation in the paraelectric phase up to a temperature by 0.5 deg higher than that of the phase transition. Energy absorption from the wave due to fluctuations in spontaneous polarization in the paraelectric phase is several time smaller than the attenuation determined in the same phase. Scattering of the wave on "needle domains" in the paraelectric phase, a mechanism proposed by O'Brien and Litovitz [2], has also to be ruled out, since the crystal had been made stress-free and subjected to permanent polarization. The enhanced attenuation of the wave by pure TGS crystals in the paraelectric phase appears to be related with the existence of an internal electric field due to the presence of crystal lattice defects. In pure TGS, the field is weak, amounting to about 5 kV/m.

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