DOMAIN STRUCTURE EFFECT ON THE PROPAGATION OF LONGITUDINAL ULTRASONIC WAVE IN PURE AND NITROANILINE-ADMIXTURED TGS CRYSTAL*

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Applying the echo method, the velocity and attenuation coefficient of longitudinal ultrasonic waves propagating in single- and multi-domain TGS crystals, pure as well as doped with ortho-, meta- and para-nitroaniline, are determined for the crystallographical directions [100], [010] and [001]. On the assumption that the wave endows the domain walls with vibrational motion, their relaxation time is determined. Also, the friction and stiffness coefficients of the walls are evaluated. TGS crystals doped with ortho-, meta- and para-nitroaniline exhibit larger variations of the velocity and attenuation coefficient due to the presence of domain walls, as well as shorter relaxation times of the walls and shorter relaxation times of spontaneous polarization than pure ones.

1. Introduction

Studies of the propagation of ultrasonic waves in TGS crystals [1–4] have revealed an anomaly of attenuation near the Curie temperature and a jump in velocity on transition of the crystal from the paraelectric to the ferroelectric phase. The anomalies are accounted for by the Landau-Khalatnikov relaxation theory [5], and the fluctuation theory of Levanyuk [6]. However, in addition to relaxation and fluctuation of the spontaneous polarization, also the domain walls characteristic for the ferroelectric state can be thought to essentially affect the propagation parameters of the ultrasonic wave, i. e. its velocity and attenuation coefficient. Regrettably, the problem has not been studied sufficiently. As yet, only one experimental paper [7] is available on the influence of domain walls on the attenuation coefficient of quasi-longitudinal ultrasonic waves during the polarizatnio switching process in these crystals. Nonetheless, there is a lack of data regarding the changes in velocity and attenuation of the wave due to the presence, in TGS crystals, of domain walls at thermodynamical equilibrium.

In the present paper, we determine the effect of domain structure on the velocity and attenuation of a quasi-longitudinal ultrasonic wave by investigating its propagation in a multi-domain, and permanently polarized, sample. We moreover determine how the effect changes when an admixture of ortho-, meta- or para-nitroaniline is introduced into the crystal lattice of TGS.

2. Results

The triglycine sulphate (TGS) single crystals used by us were grown from aqueous solution by the isothermal method. The pure and doped single crystals were grown at +43°C. Crystals doped with ortho-, meta- and para-nitroaniline were obtained from solutions containing 0.25 weight per cent of the compound. The concentrations of the admixtures in the samples was determined spectrophotometrically on extraction with ethyl ether, and were found to amount to $1.3 \cdot 10^{-4}$; $4.2 \cdot 10^{-4}$ and $2.0 \cdot 10^{-4}$ weight per cent for ortho-, meta- and para-nitroaniline, respectively.

For ultrasonic studies, we applied cubic samples with edges of 1 and 1.5 cm, in order to determine the velocity and attenuation coefficient of the wave for the three crystallographical directions [100], [010] and [001] in the same sample. For polarization, silver electrodes were deposited by evaporation in vacuum on the surfaces perpendicular to the ferroelectric axis.
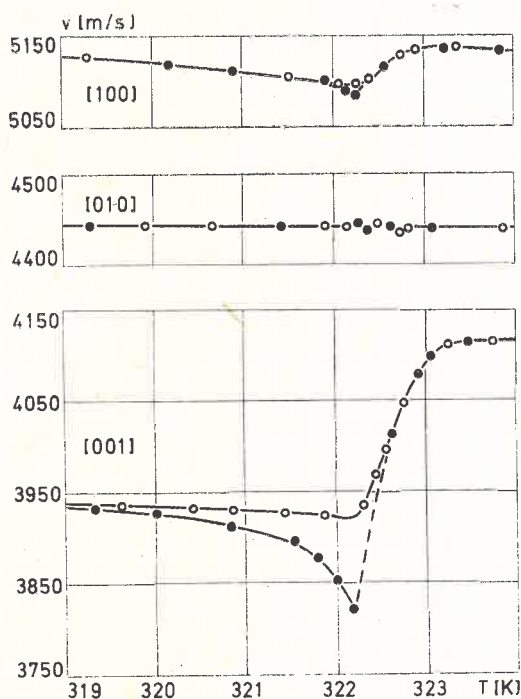

Fig. 1. Velocity of longitudinal wave in TGS crystal, for three crystallographical directions: ○ — single--domain crystal, ● — multi-domain crystal

The propagation parameters were determined by the method of ultrasonic pulse echo, at a frequency of 14.6 MHz of the longitudinal wave generated by a piezoelectric transducer. First, the parameters were determined at increasing temperature in "aged" crystals i.e. in ones having a stabilized domain structure. Next, subsequent to rejuvenation of the crystal during $10 \div 20$ hrs at $+70°C$, the measurements were repeated lowering
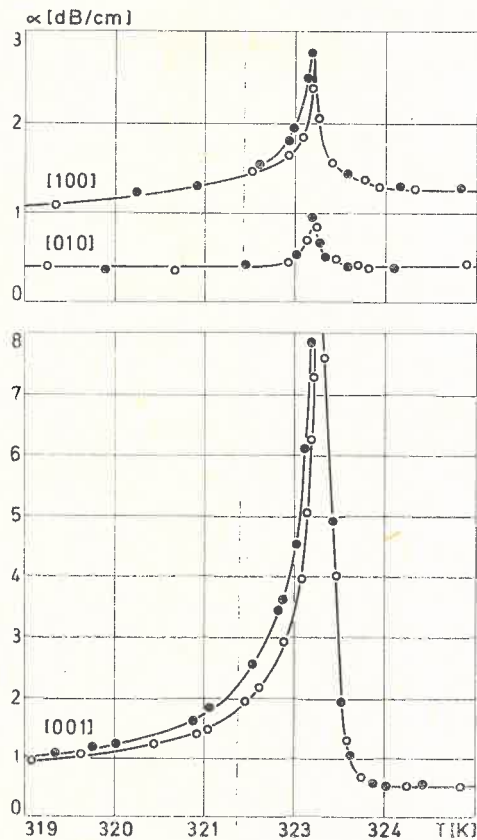

Fig. 2. Attenuation of ultrasonic wave in TGS crystal, for three crystallographical directions: ○ — single-domain crystal, ● — multi-domain crystal

the temperature down to $+20°C$. The samples were then polarized permanently, and the two parameters were once more measured at increasing temperature. In order to avoid depolarization, a field of 100 kV/m was applied to the samples during the intervals between successive measurements. The cycle of measurements ended by depolarization of the samples, which were then stored for $2 \div 3$ weeks in order to achieve re-stabilization of their domain structure. Such cycles of measurements were performed for the three crystallographical axes, both for pure and admixtured crystals.

An influence of domain walls in TGS on the velocity and attenuation coefficient of ultrasonic waves of frequency 14.6 MHz was observed only from $+45°C$ upwards. For this reason we restricted Figs 1 and 2, which show experimental temperature-charac-

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teristics of the two parameters for pure TGS in the directions [100], [010], [001], to the immediate vicinity of the Curie point.

The largest changes in propagation parameters due to domain walls were found to occur for the direction [001]. Those measured in the direction [100] were smaller. In the
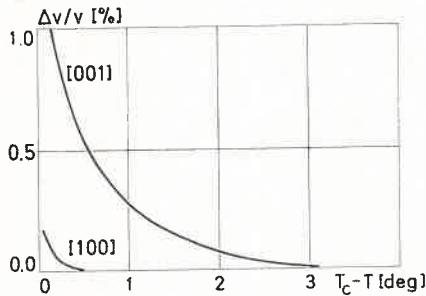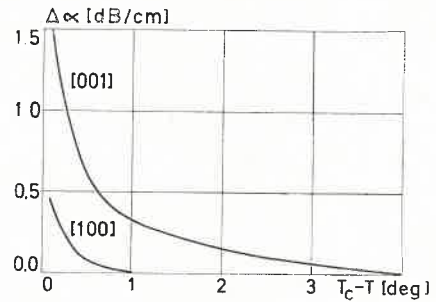

Fig. 3

Fig. 4

Fig. 3. Relative variations in acoustic wave velocity in TGS crystal due to domain walls

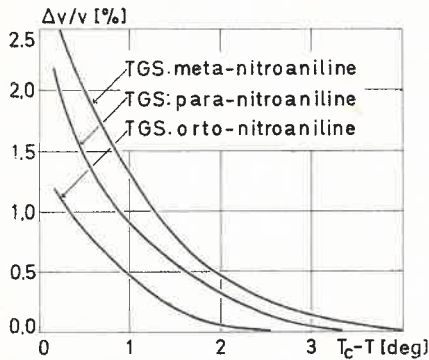Fig. 4. Variations in acoustic wave attenuation in TGS crystal due to domain walls
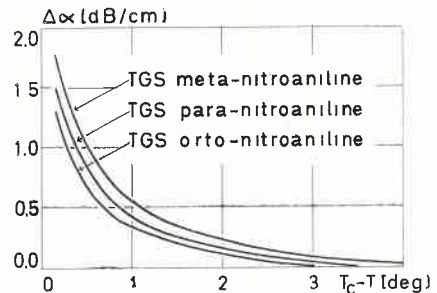

Fig. 5

Fig. 6

Fig. 5. Relative variations in ultrasonic vave welocity in TGS crystals doped with nitroanilines, for the [001] direction

Fig. 6. Variations in ultrasonic wave attenuation in TGS crystals doped with nitroanilines, for the [001] direction

direction of the ferroelectric axis, no measurable changes were noted. Obviously, this anisotropy of the domain effect is due to the geometry of the domain walls. It will be remembered that they have the shape of strongly prolate ellipsoida cylinders, extending practically throughout the entire bulk of the sample in the [010] direction, the large axis of the ellipse having the direction [100].

Figs 3 and 4 show the variations in attenuation $\alpha' - \alpha$ and relative variations in velocity $(v - v')/v$ due to the effect of domain walls in pure TGS crystals for the directions [001] and [100]. Figs 5 and 6 refer to TGS admixtured with ortho- meta- and para-nitroaniline.

3. Discussion

In a domain wall, where the spontaneous polarization changes its sign, the crystal lattice is deformed and the physical properties — in particular the acoustic impedance of the wall — differ from those of the bulk of the domain. This can lead to scattering of a plane acoustic wave on the system of domain walls. The possibility of reflection and refraction of a longitudinal elastic wave at domain walls has been discussed by Kessenich et al. [8], and the phenomenon has been confirmed experimentally in the case of $Gd_2(MoO_4)_3$ [9] and $LiNbO_3$ [10] crystals. However, in TGS the influence of domain walls on the two propagation parameters of ultrasonic waves was observed by us only from $+45°C$ upwards in spite of the fact that the heterogeneity of TGS (the ratio of the volume occupied by the walls and the volume of the crystal as a whole) amounts to 9 per cent [11] and the number of walls per unit length at room temperature differs but little from that measured at $+45°C$ [12]. This suggests that scattering of an ultrasonic wave of frequency 14.6 MHz on the domain walls of TGS crystals affects its velocity and attenuation coefficient but insignificantly.

Nonetheless, there exist another kind of interaction (beside scattering) whereby the domain walls of a ferroelectric can affect the propagation of an acoustic wave. When an ultrasonic wave propagates in a multi-domain ferroelectric, the walls immersed in the field of a time-variable deformation perform vibrational motions, leading to a change in the propagation vector of the wave i.e. its velocity and attenuation coefficient [13–15]. For the case of an elastic incident wave length much larger than the effective wall thickness $\lambda \gg d$ a weak interaction with the walls (for an attenuation path much in excess of the wavelength), Laihtman [15] derived the following dependence of the variations Δq^* of the wave vector on the parameters describing domain wall motion

$$\Delta q^* = \frac{\omega}{v} + \frac{2(hP_0)^2}{cv}\, n\, \frac{\omega}{k - i\beta\omega - M\omega^2}. \tag{1}$$

Above, P_0 is the spontaneous polarization of the bulk of the domain; h — the piezoelectric module relating the polarization and elastic stress; c — the elasticity module; n — the number of domain walls per unit length; M — the effective mass per unit surface area of the wall; β — the friction coefficient; and k — a stiffness coefficient describing the bonding of the wall to its equilibrium position. Since for crystals exhibiting no piezoelectric effect in the paraelectric phase the spontaneous strains in neighbouring domains are identical, we have neglected the influence of spontaneous strain on the wave vector in Eq. (1).

From Eq. (1), we obtain the relative change in velocity and attenuation coefficient due to the presence of domain walls as

$$\frac{\Delta v}{v} \equiv \frac{v - v'}{v} = \frac{2(hP_0)^2}{c}\, n\, \frac{k - M\omega^2}{(k - M\omega^2)^2 + \beta^2\omega^2}, \tag{2}$$

where v is the velocity in a single-domain crystal and v' that in a multi-domain one,

$$\Delta\alpha \equiv \alpha' - \alpha = \frac{2(hP_0)^2}{cv} \, n \, \frac{\beta\omega^2}{(k-M\omega^2)^2 + \beta^2\omega^2} \,, \tag{3}$$

where the prime at α has the same meaning as above.

Since the ultrasonic wave applied in this investigation has a frequency much smaller that the resonance frequency of the wall which, in TGS, amounts to $10^{10} \div 10^{11}$ s^{-1} [16]

$$\omega \ll \omega_{re} = \left(\frac{k}{M}\right)^{1/2}, \tag{4}$$

Eqs (1) and (2) reduce to

$$\frac{\Delta v}{v} = \frac{2(hP_0)^2}{c} \, \frac{n}{k} \, \frac{1}{1+\omega^2\tau^2} \,, \tag{5}$$

$$\Delta\alpha = \frac{2(hP_0)^2}{cv} \, \frac{n}{k} \tau\omega^2, \tag{6}$$

where $\tau = \beta/k$ is the relaxation time of a domain wall clamped at defects.

From Eqs (5) and (6) we obtain the relaxation time τ in the form:

$$\tau(1+\omega^2\tau^2) = \frac{v}{\omega^2} \, \frac{\Delta\alpha}{\Delta v/v} \,. \tag{7}$$

Eq. (7) involves experimentally determined quantities. Using the data of Figs 3 and 4, we calculated the relaxation time, shown as a function of temperature in Fig. 7, which moreover shows the temperature-dependence of spontaneous polarization of Ref. [17]. Clearly, at the temperature $T_c - T = 0.5$ deg the relaxation time of the domain walls is equal to that of spontaneous polarization.
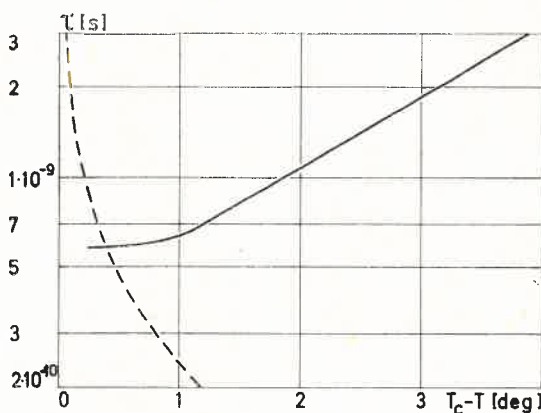

Fig. 7. Relaxation time of domain walls in pure TGS crystal. Dashed line — relaxation time of spontaneous polarization after Ref. [17]

At room temperature, the domain wall relaxation time determined from dielectric dispersion studies amounts to $10^{-6} \div 10^{-7}$ s [18-20], whence $\omega\tau = 10 \div 100$, so that the domain walls clamped on crystal lattice defects fail to keep pace with the time-variations of the acoustic field and contribute nothing to the changes in velocity and attenuation
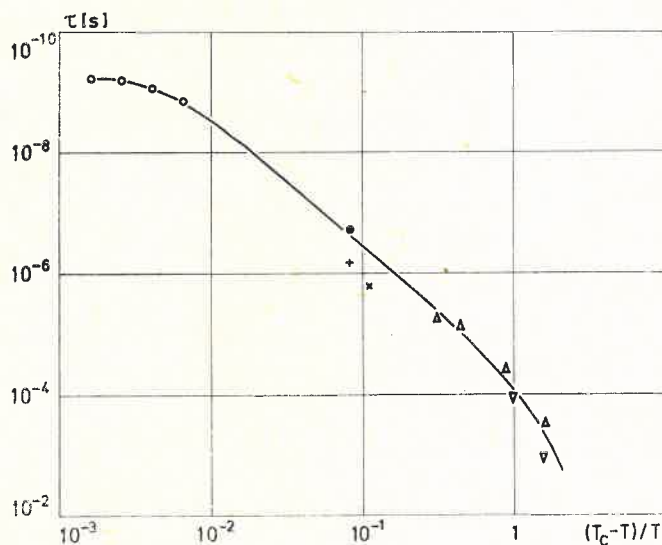

Fig. 8. Relaxation time of domain walls in pure TGS determined from ultrasonic studies and from dielectric dispersion. ○ — from ultrasonic studies and from dielectric dispersion: ● — after Ref. [18]; + — after Ref. [19]; × — after Ref. [20]; △ — after Ref. [21]; ▽ — after Ref. [22]

coefficient of the wave. In these conditions the walls have to be dealt with as rigid curtains the sole effect of which is to scatter the wave. Since the relaxation time of the defect--clamped walls determined from dielectric dispersion is equal to that of walls acted on by a weak acoustic wave, we plotted in Fig. 8 τ vs $(T_c - T)/T$ for a wide range of temperatures.

Moreover, from Eqs (5) and (6) with the condition $\omega\tau \ll 1$, one obtains the stiffness coefficient k and friction coefficient β as follows

$$k = \frac{2(hP_0)^2}{c} \, n \, \frac{1}{\Delta v/v},$$ (8)

$$\beta = \frac{2(hP_0)^2 v}{c\omega^2} \, n \, \frac{\Delta\alpha}{(\Delta v/v)^2}.$$ (9)

Taking the coefficients as: $h = 0.6 \cdot 10^9$ V/m [23], $P_0^2 = 4.8 \cdot 10^{-5} \cdot \Delta T$ C^2/m^{4}deg [24], $v = 3920$ m/s [17], $n = 3 \cdot 10^5 \cdot \Delta T^{-1/2}$ m^{-1}deg$^{1/2}$ [12, 25], we calculated k and β. In Figs 9 and 10, the coefficients k and β are plotted as functions of temperature.

The other possible interpretation of Eqs (2) and (3), i.e. for the case of free domain walls ($k = 0$), has to be rejected. In a crystal with free walls the acoustic wave velocity

would be larger than in the single-domain case, whreas the opposite is observed in our experiments.

No differences were found to occur in the velocity and attenuation values, determined at heating and cooling. This is obvious since crystals grown in the ferroelectric phase
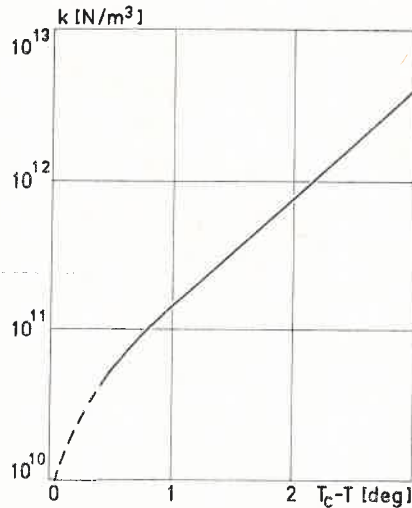

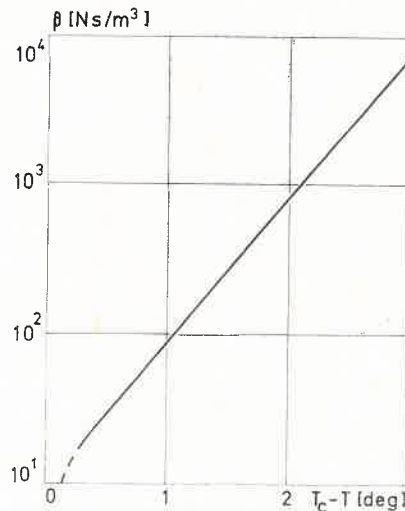Fig. 9. Stiffnes coefficient of vibrating domain walls

Fig. 10. Friction coefficient of vibrating domain walls

owing to the large number of defects, exhibit a "memory" of their domain structure [26], which is not destroyed by heating at the relatively low temperature of $+70°C$.

The TGS crystals doped with ortho-, meta- and para-nitroaniline exhibited larger changes in ultrasonic velocity and attenuation due to domain walls than pure ones.

However, the relaxation time τ (shown vs temperature in Fig. 11) is shorter than in pure crystals. Hence nitroaniline admixtures, contrary to Cu^{2+} or Cr^{3+} ions and defects introduced by irradiation, can be said not to clamp the domain structure. It is noteworthy that the relaxation time of spontaneous polarization, too, is shorter in nitroaniline-doped TGS
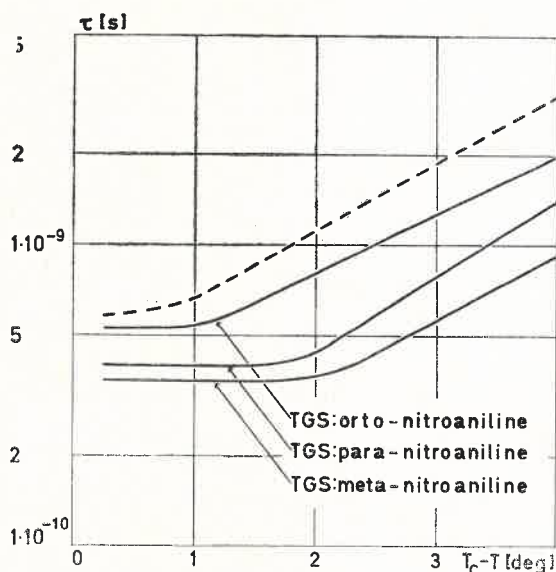
Fig. 11. Relaxation time of domain walls in TGS crystals admixtured with nitroanilines. Dashed line relaxation time in pure TGS crystals

crystals than in pure ones [17]. Also, an increase in polarization switching time has been observed for TGS crystals admixtured with nitroanilines [27]. It would be, however, unjustified to compare the results obtained by ultrasonic investigation and those of the polarization switching method, since in the latter the domain wall is detached from its clamping points and is displaced throughout the entire bulk of the sample whereas in ultrasonic and dielectric dispersion studies it performs vibrational motions without changing its position of equilibrium. Whereas the larger variations in ultrasonic wave velocity and attenuation in TGS crystals admixtured with nitroaniline can due to a stronger frittering of the domain structure.

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