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DETERMINATION OF DOMAIN WALL THICKNESS IN TGS CRYSTALS FROM MEASUREMENTS OF LONGITUDINAL ULTRASONIC WAVE PROPAGATION

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From attenuation and velocity measurements for a longitudinal ultrasonic wave, propagating in muti- and single-domain TGS crystals, the mean domain wall thickness is determined as 400÷1500 Å in the temperature interval from 318 to 322 K.

From triglycine sulphate (TGS) monocrystals, grown isothermally in ferroelectric phase, cubic samples were cut with 1 cm edges parallel to the axes [100], [010] and [001]. Silver electrodes were vacuum deposited by evaporation on the surfaces perpendicular to the ferroelectric axis. The velocity and attenuation coefficient of a longitudinal ultrasonic wave of frequency 14.6 MHz generated and received by a piezoelectric transducer were measured for the [001] direction by the echo pulse method.

The propagation parameters of the ultrasonic wave were measured from 290 to 345 K in "aged" crystals at increasing temperature and, on their rejuvenation at 345 K, at decreasing temperature. No measurable difference in velocity or attenuation was found on rejuvenation. Next, with the crystal polarized permanently, we again measured the velocity and attenuation applying a field of 100 kV/m after each measurement so as to avoid depolarization of the sample. An influence of the domain walls of TGS on the wave parameters was observed near the Curie point starting from 318 K.

The strong increase in attenuation coefficient of the longitudinal acoustic wave propagating perpendicularly to the ferroelectric axis of TGS crystal observed with increasing temperature up to the phase transition point is due to relaxation of spontaneous polarization [1]. On the other hand, the small changes in attenuation, due to fluctuation of polarization in the immediate neighbourhood of the Curie temperature, can be determined from studies of wave propagation parallel to the ferroelectric axis [2]. Moreover, the presence of

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domain walls in the ferroelectric phase can essentially modify the velocity and attenuation of longitudinal acoustic waves, propagating in TGS crystal [3].

The domain wall is a region where the spontaneous polarization changes its sign to the opposite; as a simplification, it can be assumed to be zero within the wall. As measure of the heterogeneity of the multi-domain crystal, we can apply the parameter p, defined as:

$$p = \frac{P^s - P^m}{P^s}, \tag{1}$$

where P^s is value of the polarization of the single-domain crystal, and P^m that of the sample in the multi-domain state, i. e. P^m defines value of the polarization of the space contaning domain and domain wall.

Ultrasonic wave propagation in a single-domain TGS crystal perpendicular to the ferroelectric axis is described by the relaxation equations [1]:

$$v^2 = v_P^2 - \frac{v_P^2 - v_F^2}{1+\omega^2\tau^2}, \tag{2}$$

$$\alpha = \frac{v_P^2 - v_F^2}{2v_P^3} \frac{\omega^2\tau}{1+\omega^2\tau^2}, \tag{3}$$

$$\tau = \frac{1}{2\xi L P^2}, \tag{4}$$

with v_P, v_F — the velocity in the para- and ferroelectric phase, respectively.

The ultrasonic wave propagating in ferroelectric crystal causes little disturbance of its free energy [4]. The relaxation attenuation and the change of the velocity related with interaction of the ultrasonic wave with the spontaneous polarization does not depend on the direction of the polarization vector.

We found experimentally that, in the ferroelectric phase, the velocity of the wave is lower and its attenuation coefficient higher in multi-domain crystals by comparison with single-domain ones [5]. Assuming that the elastic wave does not scatter on domain walls in TGS [6] one can explain this phenomena as a result of occupying some volume of sample by domain walls, i. e. as a result of the change of the spontaneous polarization $\Delta P = P^s - P^m$.

By insertion Eqs. (2) and (3) in Eq. (4) we obtain:

$$P^2 = \frac{v_P^2 - v^2}{2v_P^3} \frac{\omega^2}{2\xi L\alpha}. \tag{5}$$

Because the velocity and attenuation of the wave are dependent on domain structure of crystal, we can write:

$$\frac{(P^s)^2 - (P^m)^2}{(P^s)^2} = \frac{\alpha^m - \alpha^s}{\alpha^m} + \frac{\alpha^s}{\alpha^m} \frac{(v^m)^2 - (v^s)^2}{v_P^2 - (v^s)^2}, \tag{6}$$

where s and m represent respectively values of above quantities in single-domain and multi-domain states. Considering changes the single- and multi-domain states as negligible and jump in ultrasonic velocity at the Curie temperature also negligible as compared with the value of the velocity in paraelectric phase we have:

$$p = \frac{P^s - P^m}{P^s} \approx \frac{1}{2}\frac{\alpha^m - \alpha^s}{\alpha^m} + \frac{1}{2}\frac{v_F^m - v_F^s}{v_P - v_F^s}. \tag{7}$$

The parameter of the heterogeneity can as well be re-defined as:

$$p = \frac{\bar{S} \cdot \bar{d}}{\bar{V}}, \tag{8}$$

with: $\bar{S}$ — the mean surface area of a wall; $\bar{d}$ its mean thickness; and $\bar{V}$ the mean volume of domain. On the assumption of planar walls in the (001) plane, the latter definition simplifies to:

$$p = \frac{\bar{d}}{\bar{w}}, \tag{9}$$

where $\bar{w}$ is the mean width of domain.

Fig. 1 shows the heterogeneity of TGS crystals determined from the temperature-variations of attenuation coefficient and velocity of the wave.

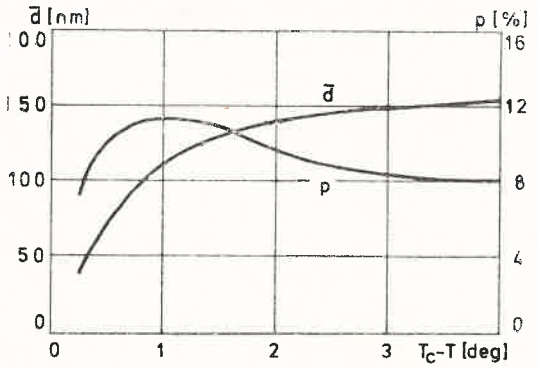

Fig. 1. Parameter of heterogeneity and mean domain wall thickness of multi-domain TGS crystals

In order to determine the domain wall thickness, we need moreover to have available the mean width of the domains. Assuming the latter as $\bar{w} = 10^{-4}$ cm at the temperature $T_c - T = 1$ deg (being the average of the values reported by various authors [7–11]) and a temperature-dependence given by $\bar{w} \sim \sqrt{T_c - T}$ in the temperature interval studied [7, 8], we determined the mean thickness of domain walls in TGS crystal as shown in Fig. 1 as a function of temperature.

It is highly interesting that, contrary to other ferroelectric crystals, the domain wall thickness in TGS decreases with increasing temperature up to the Curie point throughout

the entire temperature range investigated by us. The same trend of the wall thickness versus temperature has been reported for TGS crystals by Šafrankova [12] and Stankowska [13]. It is worth adding that the wall thickness of 400–1500 Å, determined by us from measurements of ultrasonic wave propagation, is in agreement with the results of others [12–15].

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