

THE INFLUENCE OF THE ELECTRIC FIELD AND THE DOMAIN STRUCTURE ON THE ULTRASOUND ABSORPTION IN TRIGLYCINE SULPHATE

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The paper presents the results of ultrasonic attenuation measurements on single crystals of ferroelectric TGS. Attenuation has been studied in the vicinity of the transition temperature, as a function of the applied electric field. It has been proved, that domain walls contribute to sound absorption.

I. INTRODUCTION

The absorption of quasi-longitudinal ultrasonic waves in ferroelectric crystals of triglycine sulphate (TGS) has been studied in Refs. [1, 2, 3, 4, 5] as a function of temperature and frequency. It is well known that the absorption coefficient shows an anomalous increase when the transition temperature T_0 is approached. If a d. c. electric field is applied in the y -direction (which is the ferroelectric axis), the phase transition disappears [6] but the anomalous increase of α still exists and the character of its temperature dependence can be strongly influenced by the applied field.

The aim of this paper is to investigate the α vs. field dependence in more detail. Two different procedures have been used: a) absorption measurements during the polarization reversal process existed by a d. c. applied field; in this case, the domain walls influence on α can be evaluated.

b) absorption measurements on a single domain crystal, as a function of the applied field. In both cases the absorption coefficient is applied to a quasi-longitudinal wave coupled to the polarization along the ferroelectric axis.

II. ULTRASOUND ABSORPTION DUE TO DOMAIN WALLS

It was suggested for the first time by O'Brien and Litowitz [1] that the domain walls in a ferroelectric crystal may enhance the ultrasonic absorption.

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In order to prove this and to find the magnitude of this effect, the best experiment would be to measure α as a function of the number n of the domain walls in the specimen under the condition, of a zero applied field. A suitable technique was used previously [7] by one of the authors for the study of the permittivity as a function of n : the average polarization and n can be changed step by step by discharging a capacitor into the sample under investigation. It was found in the present study, however, that in large samples required for ultrasonic measurements, considerable backswitching exists which makes this method unpractical. We have, therefore, adopted the method of measuring α as a function of time during a polarization reversal process excited by a strong d. c. electric field.

The TGS samples with $T_c = 49^\circ\text{C}$ were cut from crystals grown by Dr. B. Březina [8] and had the shape of parallelepipeds with sides along the crystal axes: $L_x = L_y = 1\text{ cm}$, $L_z = 1.5\text{ cm}$. The pulse echo method has been used as a generator and as a receiver. A sonic wave with a diameter of 0.7 cm) serving both was sent into a delay line to the other side of which the TGS sample was attached by a wax bond in such a way that the wave propagated along its Z -axis. In this system there are two sources of echoes: 1. Reflection from the boundary between the samples and the delay line; 2. Reflection from the free face of the sample. Supposing the first reflection does not change during the measurement process, the change of α to be measured can be evaluated

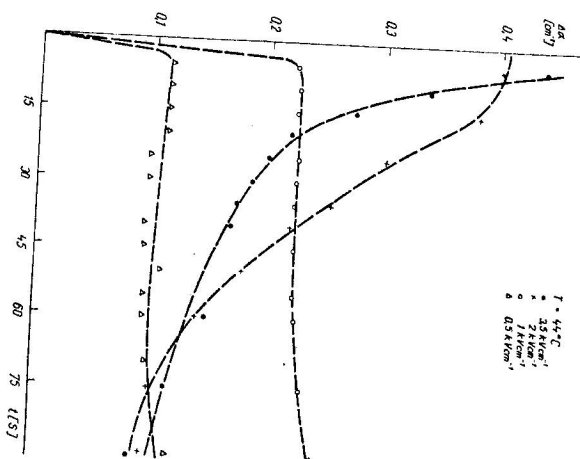


Fig. 1. Attenuation change as a function of time during the polarization reversal process at $T = 44^\circ\text{C}$ for different switching fields.

from the amplitudes of the second kind echoes. If it does change, we can eliminate this effect by considering the first kind echoes.

The two faces perpendicular to the y -axis were provided with gold evaporated electrodes. The measurement procedure was as follows. First, a d. c. field of 3.5 kV/cm was applied along the y -axis for 15 minutes so that a single domain state was achieved. This field was then continuously decreased to the required E_s value (e. g. $E_s = 1\text{ kV/cm}$) and then its polarity was suddenly reversed. This excites the switching process during which the number of domain walls first increases, reaches a maximum and approaches zero again [6], the final state corresponding to the reversed direction of the spontaneous polarization.

Figs. 2 and 3 show the increase $\Delta\alpha$ of attenuation as a function of the time t

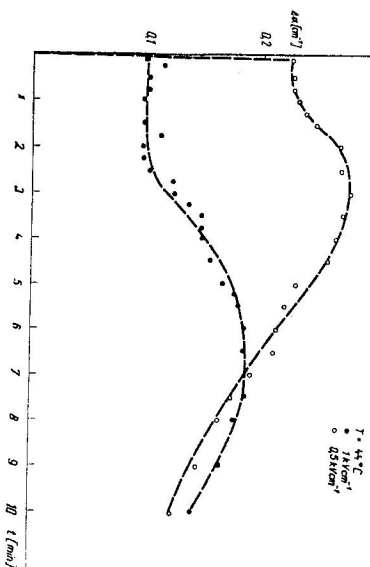


Fig. 2. Time dependence of the attenuation increase at $T = 44^\circ\text{C}$. Time scale is different from that in Fig. 1.

elapsed since the beginning of switching, for $T = 44^\circ\text{C}$. The first value was taken at $t = 5\text{ sec.}$; it can be seen that while for $E_s = 3.5\text{ kV/cm}$ and 2 kV/cm the maximum of $\Delta\alpha$ occurs at $t_m < 5\text{ sec.}$, for $E_s = 1\text{ kV/cm}$ and 0.5 kV/cm it sets in a $t_m = 3\text{ min.}$ and 7 min. , resp. For higher temperatures t_m decreases: at $T = 45.8^\circ\text{C}$ and $E_s = 1\text{ kV/cm}$, $t_m \approx 10\text{ sec.}$, as seen from Fig. 4.

While the detailed shape of the $\Delta\alpha$ vs. t curve changes from sample to sample and may not be reproduced even on different specimens, the following features occur repeatedly: t_m increases and $\Delta\alpha_{max}$ decreases with decreasing E_s ; for constant E_s , t_m decreases with T approaching T_c . This behaviour closely resembles that of the permittivity enhancement measured during the switching process [9] and is also similar to the properties of the switching current. It is known from the theories of switching [10] that the number of domains and consequently also the total wall area S_w per unit volume show first a rise and reach a maximum with subsequent decay during switching.

Thus there is no doubt that the attenuation enhancement described above is due to the scattering of energy on the domain walls.

It cannot be, however, concluded that $\Delta\alpha$ is proportional to S_w . While it is not the purpose of this paper to analyze the scattering processes in detail, we want to show here that there are at least two mechanisms through which $\Delta\alpha$ is effected by domain walls.

1. Within the domain wall, where the polarization P_s changes its direction, the crystal lattice is deformed. Recent measurements and theoretical considerations [11] show the domain wall in TGS to be unusually thick (2400 Å at

$T = T_c - 5^\circ$). It may, therefore, be considered that the acoustic impedance of the wall differs from that of the domain bulk. Then we can expect multiple reflections of sound waves leading to $\Delta\alpha$ which is not proportional to S_w .

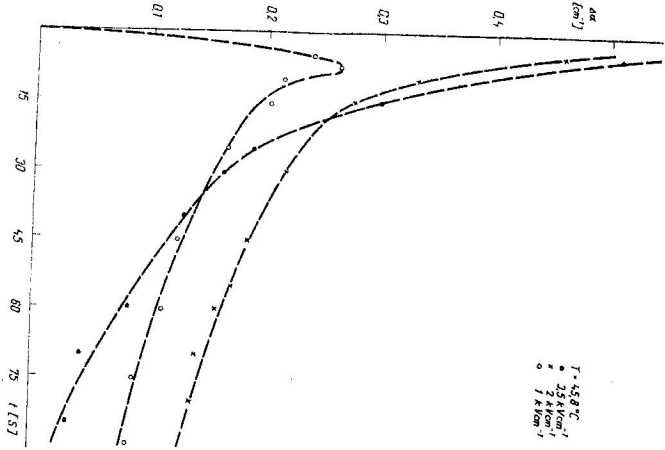


Fig. 3. Attenuation increase during switching at $T = 45.8^\circ\text{C}$.

2. The sound wave energy may be absorbed in the domain wall itself and in the following there is a simple model accounting for it on a macroscopic scale. Suppose a longitudinal wave propagating along the Z -axis so that the only non-zero component of the strain tensor is

$$\epsilon_{33} = \epsilon_{33}^0 \cos(\omega t - kz). \quad (1)$$

Due to piezoelectric coupling, a polarization wave accompanies the sound wave, so that we can write [1]

$$P_2 = g_{233}\epsilon_{33} \quad (2)$$

where g_{233} is a relaxational piezoelectric coefficient. Now, (see, e. g., Samikov's treatise [12]) the dissipative function is usually written in the form

$$\Psi = \frac{1}{2} \eta_{ijkl} \dot{\epsilon}_i \dot{\epsilon}_j \dot{\epsilon}_k \dot{\epsilon}_l + \frac{1}{2} \mu_{ij} \dot{P}_i \dot{P}_j \quad (3)$$

where the dot means a time derivative and the cross-terms are neglected. From this, considering that for the acoustic energy U we have [13]

$$dU/dt = -2 \int \Psi dV, \quad (4)$$

the absorption coefficient defined as

$$\alpha = -\frac{1}{vU} \langle dU/dt \rangle \quad (5)$$

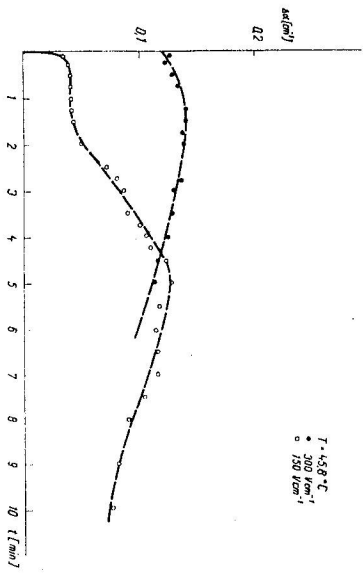


Fig. 4. Attenuation increase at $T = 45.8^\circ\text{C}$ during switching excited by a low field.

can be calculated, where v is the sound wave velocity. We want to suggest that if a ferroelectric crystal consists of conversely polarized domains, another variable should be introduced in addition to ϵ_{ij} and P_i , namely $\partial P_i / \partial x_j$, which acquires high values as compared to the single domain case. This can be seen from the following argument: Since g_{233} is an odd-rank tensor, it is clear that it differs in sign in two neighbouring domains. Thus a given deformation ϵ_{33} causes, according to Eq. (2), induced polarization components which differ in sign on the two sides of the domain wall. If the domain wall located at Z has a thickness d , the jump of the induced polarization across this distance is

$$\Delta P_2 = g_{233}\epsilon_{33}(z + d) - (-g_{233})\epsilon_{33}(z). \quad (6)$$

Since $d \ll \lambda \approx 70\mu$ the value of $\partial P / \partial z$ inside the wall can be approximated by $\Delta P_2 / d$. Then, from (1) and (6), we have

$$(\partial^2 P_2 / \partial z^2)_{wall} = -\frac{2g_{233}\omega\epsilon_{33}^{(0)}}{d} \cos \frac{\pi d}{\lambda} \sin \left(\omega t - kz - \frac{\pi d}{\lambda} \right) \quad (7)$$

inside the wall, while the same quantity within the domain or in a single domain crystal would be given by

$$(\partial^2 P_2 / \partial z \partial t)_{\text{wall}} = \frac{2g_{kz2}\omega e_{33}^{(0)}}{\lambda/\pi} \cos(\omega t - kz).$$

For $d \ll \lambda$, obviously, $(\partial^2 P_2 / \partial z \partial t)_{\text{wall}} \gg (\partial^2 P_2 / \partial z \partial t)_{\text{bulk}}$ so that the latter can be neglected.

Thus in a multidomain crystal the dissipation function acquires an additional term

$$\Delta \Psi = \frac{1}{2} \delta_{332} (\partial^2 P_2 / \partial z \partial t)_{\text{wall}}^2, \quad (8)$$

where δ_{332} is a component of the viscosity tensor. The cross terms have again been neglected. Calculating $\langle 2 \int \Psi dV \rangle$ on the assumption that here are N domain walls per unit volume and putting

$$U = \frac{1}{2} \rho v^2 \epsilon_{33}^{(0)2}, \quad (9)$$

where ρ denotes the density, we get from (5) the following expression for the increase of the attenuation coefficient due to the domain walls:

$$\Delta \alpha = \frac{4\delta_{332} g_{kz2}^2}{\rho v^3} \frac{\cos^2(\pi d/\lambda)}{d} N_{01}^2. \quad (10)$$

While it is clear that $\Delta \alpha$ is proportional to N , its temperature dependence cannot be easily resolved, since a number of quantities involved may depend on temperature: δ , g , d , N . Experimentally, we have observed that for an increasing T the domain wall influence on $\Delta \alpha$ becomes more pronounced.

The procedure outlined above, leading to $\Delta \alpha \sim N$, is of course a very rough approximation. Introducing $(\partial^2 P / \partial z \partial t)$ as a new variable into the dissipation function is somewhat analogous to considering the term proportional to $(\partial P / \partial z)^2$ in the free energy of a multidomain crystal.

III. INFLUENCE OF THE ELECTRIC FIELD ON THE ABSORPTION IN SINGLE-DOMAIN TGS

In this section we suppose an electric field E to be applied along the ferroelectric axis of TGS so that the crystal becomes a single-domain one and electrically biased. For the case when a longitudinal sound-wave of the frequency ω propagates in the k -direction, the following expression for the free energy coefficient has been derived by Baják [5]:

$$\alpha_E = \frac{2g_{kz2}}{v c_{kzk}^P (\xi^s + E/2P_s)} \frac{\omega^2 \tau_E}{1 + \omega^2 \tau_E^2}. \quad (11)$$

Here g_{kz2} is the electrostriction coefficient coupling the compression along k with the polarization component P_2 , C_{kzk}^P is the elastic modulus as the constant P . The saturation constant of a clamped crystal is denoted by ξ^s and P_E stands for the polarization induced by biasing field E . The relaxation time is given by [5]

$$\tau_E = \left[\gamma \left(2\xi^s P_E^2 + \frac{E}{P_E} \right) \right]^{-1}, \quad (12)$$

where γ is the kinetic coefficient. If the field E is applied at constant stress (free crystal), the following holds [6]

$$E = \chi P + \xi^s P^3, \quad (13)$$

ξ^s being the saturation constant as constant stress, χ the reciprocal susceptibility. Let us denote by α_0 , τ_0 , P_s the values of α_E , τ_E , or P_E , resp., for $E \rightarrow 0$. At $T < T_c$, it follows from (13) that $E/P_E = \xi^s (P_E^2 - P_s^2)$. Introducing this relation into Eq. (11) we can derive the following expression:

$$\frac{\alpha_0}{\alpha_E} = \frac{2\xi^s P_E^2 + \xi^s (P_E^2 - P_s^2)}{2\xi^s P_E^2} \frac{\tau_0}{\tau_E} \frac{1 + \omega^2 \tau_E^2}{1 + \omega^2 \tau_0^2} \quad \text{at } T < T_c. \quad (14)$$

For $\omega^2 \tau_0^2 \ll 1$ and $\omega^2 \tau_E^2 \ll 1$ this can be rewritten by considering Eq. (12) in the form

$$\frac{\alpha_0}{\alpha_E} = \left[\frac{P_E}{P_s} + \frac{1}{2} \frac{\xi^s}{\xi^s} \left(\frac{P_E}{P_s} - \frac{P_s}{P_E} \right) \right]^2 \quad \text{at } T < T_c. \quad (15)$$

In the paraelectric phase and for low biasing fields ($\xi^s P_E^2 \ll \chi$, i. e. $E = \chi P$), the following expression has been obtained in Ref. [5]:

$$\alpha_E = \frac{4g_{kz2}\omega^2 P_E^2}{v c_{kzk}^P \gamma^2} = \frac{4g_{kz2}\omega^2 P_s^4}{v c_{kzk}^P \gamma E^2} \quad \text{at } T > T_c. \quad (16)$$

All the preceding formulae of this section apply to a single-domain crystal. Experimentally, this state was achieved by prepoling a TGS sample prior to the measurements of α vs. the applied field. The experimental arrangement was the same as in the previous section. Fig. 5 shows the attenuation change $\Delta \alpha$ as a function of E at temperatures below T_c . Considering Eq. (15), these curves can be used to evaluate the quantity P_E/P_s as a function of E . For two different temperatures, the results are plotted in Fig. 6 (full lines). The same dependence can also be calculated from the thermodynamic potential (Eq. (13)) and the obtained values are also included in Fig. 6 (broken lines). Considering the very indirect way of determining P_E/P_s from ultrasonic absorption, the is satisfactory.

Due to the tendency of backswitching, the crystals may not be completely single domains neither at the beginning for $E = 0$ nor during the measuring process. This is the most probable cause of discrepancies between the two sets of curves.

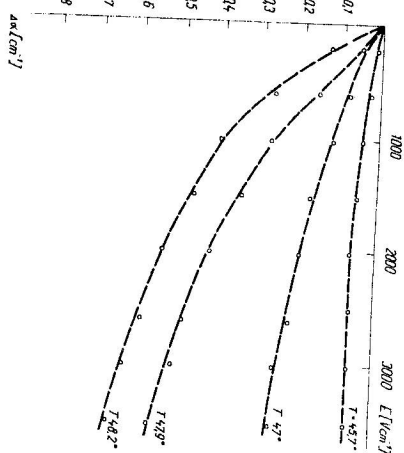


Fig. 5. Attenuation change due to the electric field E as a function of E for a single-domain crystal at temperature below T_c .

Above the Curie point, the experimental data are shown in Fig. 7. Again, this behaviour is in a quantitative agreement with Eq. (16). For a constant T , P_E increases with E and thus α also increases. As α constant E , P_E decreases with rising temperature, which results in a decrease of α .

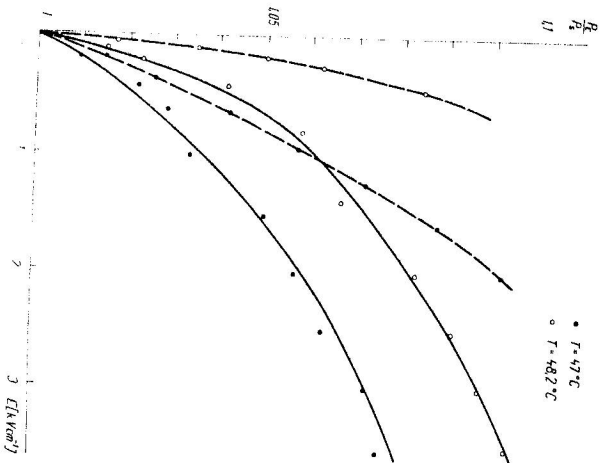


Fig. 6. The dependence of P_E/P_0 on the electric field as calculated from the attenuation data (full lines) and from the thermodynamic potential (broken lines) for two different temperatures. The following values have been used for numerical calculations: $\chi = 3.92 \times 10^{-3}$ ($T = 49.0$) c. g. s. u.; $\xi^0 = 8.0 \times 10^{-10}$ c. g. s. u.; $\xi^c = 12.2 \times 10^{-10}$ c. g. s. u.

On a microscopic scale, the decrease in absorption due to the applied field at $T < T_c$ can be explained as being the consequence of the relaxation time behaviour (cf. Eq. (12)): the time constant τ_E of restoring the long-range equilibrium, shortens with E . For $T > T_c$, on the other hand, a rising electric field intensifies the interaction between the sound wave and the crystalline lattice which results in an increase of the attenuation. It may be noted, however, that the O'Brien and Litovitz approach, on which Baják's consideration is based, gives zero attenuation for $T > T_c$ and $E = 0$. As it has been pointed out by Dvořák [14], polarization fluctuations when properly taken into account, would give a finite α even in the paraelectric phase. In this sense the formulae given above are approximative.

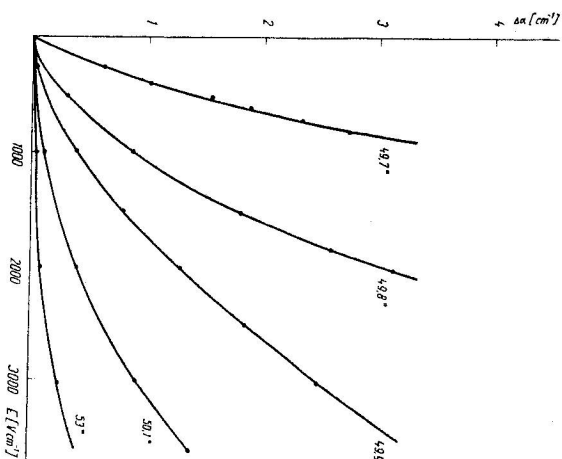


Fig. 7. Attenuation change due to the electric bias at temperatures above T_c .

IV. SUMMARY

The attenuation α of quasi-longitudinal sound waves of $f = 58$ MHz has been studied in TGS single crystals at temperatures close to transition point T_c . The experimental arrangement made it possible to measure α for waves piezoelectrically coupled with polarization along the ferroelectric axis, as a function of the electric field E applied along this axis.

In the ferroelectric phase the attenuation is strongly influenced by the domain walls as proved by observing attenuation transients during the polarization reversal process. For a single domain crystal, α is a decreasing function

of E . The situation is reversed in the paraelectric phase, where E causes α to increase. The behaviour of single domain crystals can be explained on the basis of the O'Brien and Litovitz theory [1] extended by one of the authors [5] to the case of a present biasing field.

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