

THE INFLUENCE OF THE ELECTRIC FIELD ON THE ULTRASONIC ATTENUATION IN FERROELECTRIC TRIGLYCINE SULPHATE

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The attenuation of quasi-longitudinal ultrasonic waves in the Z -direction of a single crystal of triglycine sulphate is investigated in the case when the electric field is applied to the sample in the direction of its polar axis Y . The applied electric field changes the relaxation time associated with the approach of the long range order to equilibrium and according to this one changes the ultrasonic attenuation. The measurement of the temperature dependence of the attenuation of quasi-longitudinal ultrasonic waves with the frequency of 58 Mc/s have been made in the Z -direction of a single crystal of TGS to which an electric field of intensities of 0 V/cm, 1 kV/cm and 3.5 kV/cm was applied. A qualitative agreement between theory and the experimental results was found.

1. INTRODUCTION

Ultrasonic measurements near a second order phase transition in a ferroelectric material show that the attenuation of the ultrasound increases rapidly when the temperature approaches the transition point [1], [2], [3], [4]. The second-order phase transition in ferroelectrics is characterized by a discontinuity of the first derivative of polarization with respect to temperature at the Curie point and the anomalous increase of ultrasonic attenuation is explained by the hyperbolical increasing of the relaxation time associated with the approach of the long range order to equilibrium.

The electric field applied in the direction of the polar axis of the ferroelectric material, which undergoes the second-order phase transition, induces in the material polarization without the discontinuity of its first derivative and the second-order phase transition disappears. The measurement of ultrasonic attenuation shows that the increase of attenuation exists also in the above mentioned case, but the maximum of attenuation decreases with the increase of the applied electric field.

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In the present paper we investigate the attenuation of quasi-longitudinal waves in triglycine sulphate (TGS) in the case when an electric field is applied to the sample in the direction of the polar axis Y . We generalize the theory presented by O'Brien and Litovitz [1] to the above mentioned case and we give the results of the measurements of the dependence of attenuation of quasi-longitudinal ultrasonic waves on temperature in a sample of TGS to which an external electric field was applied in the Y direction.

II. THEORY

In the following discussion we extend the theory of O'Brien and Litovitz [1] to the case when the external electric field is applied to a sample of TGS in the direction of its polar axis Y .

According to [1] the Devonshire free energy for TGS can be written in the form:

$$F = \frac{1}{2} \sum c_{ij}^p \epsilon_j \epsilon_j + \sum g_2 \epsilon_j P_2^2 + \frac{1}{2} \chi P_2^2 + \frac{1}{4} \xi P_2^4, \quad (1)$$

where c_{ij}^p are the elastic constants for the constant P , g_2 are the constants which express the coupling of the stress tensor components σ_j to the polarization P_2 in the direction of the polar axis Y , χ and ξ are coefficients.

The components of the stress tensor σ_K corresponding to the strain component ϵ_K can be written as:

$$-\sigma_K = \frac{\partial F}{\partial \epsilon_K} = \sum c_{Kj}^p \epsilon_j + g_{K2} P_2^2. \quad (2)$$

The intensity of the electric field in the Y -direction is:

$$E_2 = \frac{\partial F}{\partial P_2} = 2 \sum g_j g_2 P_2 + \chi P_2 + \xi P_2^3. \quad (3)$$

Assuming that the longitudinal sound wave is spreading in the K -direction of the crystal, i. e. $\epsilon_K \neq 0$, $\epsilon_j = 0$ for $j \neq K$ and assuming that the wave causes small fluctuations of P_2 and ϵ_K about their equilibrium values P_E and ϵ_K^0 , the intensity of the applied electric field becomes:

$$E = 2 \sum g_j \epsilon_j^0 P_E + \chi P_E + \xi P_E^3. \quad (4)$$

Equation (4) can be written as:

$$E = a P_E + \xi P_E^3. \quad (5)$$

From (1) and (3) we have:

$$-\dot{\sigma}_K = c_{KK}^p \dot{\epsilon}_K + 2g_{K2} P_E \dot{P}_2 \quad (6)$$

$$\frac{\partial \dot{F}}{\partial P_2} = 2 \sum g_{\varepsilon} \varepsilon_j^0 \dot{P}_2 + 2g_{K\varepsilon} \varepsilon_K P_E + \chi \dot{P}_2 + 3\varepsilon P_E^2 \dot{P}_2. \quad (7)$$

We can derive from (4) and (7) the relation:

$$\frac{\partial \dot{F}}{\partial P_2} = 2g_{K\varepsilon} \varepsilon_K P_E + \left(2\varepsilon P_E^2 + \frac{E}{P_E} \right) \dot{P}_2. \quad (8)$$

If we introduce the kinetic equation in the form:

$$\frac{\partial F}{\partial P_2} = -\frac{1}{\gamma} \dot{P}_2 \quad (9)$$

and if we assume that \dot{P}_2 vary sinusoidally with the ultrasound frequency ω , the equations (8) and (9) give

$$-\frac{i\omega}{\gamma} \dot{P}_2 = 2g_{K\varepsilon} \varepsilon_K P_E + \left(2\varepsilon P_E^2 + \frac{E}{P_E} \right) \dot{P}_2. \quad (10)$$

The relaxational piezoelectric constant from (10) is:

$$g_{K\varepsilon} = \frac{\dot{P}_2}{\varepsilon_K} = -\frac{1}{1 + i\omega \left[\gamma \left(2\varepsilon P_E^2 + \frac{E}{P_E} \right) \right]^{-1}}, \quad (11)$$

where the relaxation time is:

$$\tau = \left[\gamma \left(2\varepsilon P_E^2 + \frac{E}{P_E} \right) \right]^{-1}. \quad (12)$$

For the complex elastic constant \tilde{c}_{KK} we can obtain from (6), (11), and (12) the expression:

$$\tilde{c}_{KK} = -\frac{\dot{\sigma}_K}{\dot{\varepsilon}_K} = c_{KK}^P - \frac{2g_{K\varepsilon}^2}{\left(\xi + \frac{E}{2P_E^3} \right)} \frac{(1 - i\omega\tau)}{(1 + \omega^2\tau^2)}. \quad (13)$$

The coefficient of the ultrasonic attenuation expressing the exponential decrease of the wave energy is defined as [6]:

$$\alpha = \left| \frac{1}{U} \left\langle \frac{dU}{dx} \right\rangle \right| = \left| \frac{1}{Uv} \left\langle \frac{dU}{dt} \right\rangle \right|, \quad (14)$$

where U is the acoustical energy, $\langle dU/dx \rangle$ and $\langle dU/dt \rangle$ are the average changes

of U per centimeter and second, respectively, and v is the velocity of the ultrasonic wave.

When all the acoustic energy is in the form of potential energy it has the value:

$$U = \frac{1}{2} \max (\text{Re} \varepsilon_K \cdot \text{Re} \sigma_K) = \frac{1}{2} \text{Re} \tilde{c}_{KK} \varepsilon_{0K}^2, \quad (15)$$

where $\text{Re } f$ is the real part of f and ε_{0K} is the amplitude of the deformation change. Deriving (15) we have used $-\sigma_K = \tilde{c}_{KK} \varepsilon_K$.

According to the rule for the average of product of the real part of two sinusoidal factors: $\langle \text{Re} A \cdot \text{Re} B \rangle = \frac{1}{2} \text{Re}(A \cdot B^*)$, the average rate of the change of energy can be written as:

$$\left| \left\langle \frac{dU}{dt} \right\rangle \right| = |\langle \text{Re} \tilde{c}_{KK} \varepsilon_K \cdot \text{Re } i\omega \varepsilon_K \rangle| = \left| \frac{\text{Im} \tilde{c}_{KK} \omega \varepsilon_{0K}^2}{2} \right|, \quad (16)$$

where $\text{Im} \tilde{c}_{KK}$ is the imaginary part of \tilde{c}_{KK} . From (14), (15) and (16) we obtain:

$$\alpha = \frac{\omega}{v} \frac{\text{Im} \tilde{c}_{KK}}{\text{Re} \tilde{c}_{KK}}. \quad (17)$$

Using (13) α becomes:

$$\alpha = \frac{2g_{K\varepsilon}^2}{v \left(\xi + \frac{E}{2P_E^3} \right)} \cdot \frac{\omega^2 \tau}{c_{KK}^P (1 + \omega^2 \tau^2) - 2g_{K\varepsilon}^2 \left/ \left(\xi + \frac{E}{2P_E^3} \right) \right.}, \quad (18)$$

and assuming that

$$\frac{2g_{K\varepsilon}^2}{\left(\xi + \frac{E}{2P_E^3} \right)} \ll c_{KK}^P \quad (19)$$

we have

$$\alpha = \frac{2g_{K\varepsilon}^2}{vc_{KK}^P \left(\xi + \frac{E}{2P_E^3} \right)} \frac{\omega^2 \tau}{1 + \omega^2 \tau^2}. \quad (20)$$

The relations (12) and (20) characterize the relaxation damping of ultrasonic waves in TGS to which the electric field is applied in the direction of the polar axis Y . We can see that the relaxation time (12) increases with increasing temperature, it reaches its maximum and then decreases. We also can see the increase of ultrasonic attenuation in the vicinity of temperature at which the equilibrium value of polarization is $P_E^3 = E/4\xi$.

For temperature $T < T_c$, where T_c is the Curie temperature, $P_E \rightarrow P_s$ if $E \rightarrow 0$. The spontaneous polarization P_s fulfils equation (5) at $E = 0$ and we have

$$P_s^2 = -\frac{\alpha}{\xi}. \quad (21)$$

The relations (12) and (20) can be now rewritten

$$\tau = [\gamma\xi(3P_E^2 - P_s^2)]^{-1} \quad (22)$$

$$\alpha = \frac{4g\kappa_2^2 P_E^2}{v\kappa_K \xi(3P_E^2 - P_s^2)} \frac{\omega^2 \tau}{1 + \omega^2 \tau^2}. \quad (23)$$

The limit $E \rightarrow 0$, $P_E \rightarrow P_s$ for $T < T_c$ in (22) and (23) leads to equations derived by O'Brien and Litovitz.

If we put $P_s = P_E - \Delta P$ and $P_s^2 = P_E^2 - 2P_E \Delta P$, the relations (22) and (23) for $\omega^2 \tau^2 \ll 1$ give

$$2P_E - P_s = \frac{|g\kappa_2|\omega}{(v\kappa_K \gamma)^{1/2} \xi} \left(\frac{1}{\alpha} \right)^{1/2}. \quad (24)$$

The relation (24) allows us to compute P_E from α if we know P_s and the constants belonging to (24).

For the temperature $T > T_c$ the spontaneous polarization $P_s = 0$ and $\alpha = 0$ if $E = 0$. The applied electric field induces P_E , which decreases with increasing temperature (5).

If $2\xi P_E^2 \ll E$ and $\omega^2 \tau^2 \ll 1$, we have from (12) and (20) the relations

$$\tau = \frac{P_E}{\gamma E}, \quad (25)$$

$$\alpha = \frac{4g\kappa_2^2 \omega^2}{v\kappa_K \gamma E^2} P_E^4. \quad (26)$$

according to which we can compute P_E .

Concluding the discussion we must say that the above solution is acceptable for a single domain crystal of TGS. The influence of the domain walls was not taken into account. Moreover, the analysis is based on the assumption that the acoustical wave is planar and longitudinal, and propagating in an infinite crystal; therefore the effect of „clamping“ of the crystal need not be considered. The constant ξ^* has been defined by equation (1) under the assumption of the value at a constant strain and we require the constant strain value

of ξ^* also in equations (21) to (24). In practice, however, it is difficult to suppress the spontaneous polarization [5] and most experiments were done using samples with „unclamped“ spontaneous polarization. In applying the relations (21) to (24) to such an experimental situation, it is necessary, as we do in [9], to modify these relations so as to account for the experimental conditions of an „unclamped“ spontaneous polarization.

III. EXPERIMENTAL PROCEDURE AND RESULTS

The measurements of the temperature dependence of the attenuation of quasi-longitudinal ultrasonic wave have been made in the Z -direction (5) of a single crystal of TGS on which an external electric field of intensities of 0 V/cm, 1 kV/cm and 3.5 kV/cm was applied in the direction of the polar axis Y .

The samples of TGS had dimensions of $L_x = 1$ cm, $L_y = 1$ cm and $L_z = 1.5$ cm, where L_x , L_y and L_z are the lengths of the edges of the samples in the direction of the X , the Y and the Z axes, respectively.

Pulse-echo attenuation measurements were made with the one-probe method. The X -cut quartz disk with a diameter of 0.7 cm bonded with silicon oil was used to generate the longitudinal ultrasonic waves and to receive them. The ultrasonic waves entered the TGS single crystal either through the X -cut quartz transducer bonding directly the investigated sample or through the fused silica delay line. The directly bonding transducer was used in measurements with $E = 0$ V/cm. When the transducer was bonded directly to the sample of TGS, the golden grounded electrode was evaporated on its face. The grounding of this electrode must be carefully performed, since any electric waves penetrating into the sample generate in it ultrasonic waves which interfere with the waves generated by the transducer and this fact distorts the measured value of attenuation. The delay line was used in the case of an applied electric field. The change of absorption was measured in this case only and the coefficient of attenuation was computed from results obtained without the field.

The long time stability of temperature was better than $\pm 0.05^\circ\text{C}$ and the accuracy of temperature measurements was better than $\pm 0.1^\circ\text{C}$.

Fig. 1 shows the frequency dependence of attenuation of quasi-longitudinal ultrasonic waves in the Z -direction of TGS at room temperature. We can see that $\alpha \sim f^2$. The deflection of the measured value α from this dependence at lower frequencies can be explained by increasing diffraction losses with decreasing frequency (7). Hence we have chosen 58 Mc/s for performing all further measurements.

Fig. 2 shows the dependence of α vs. T at $E = 0$ V/cm and in Table 1 are the corresponding values α , T , and E .

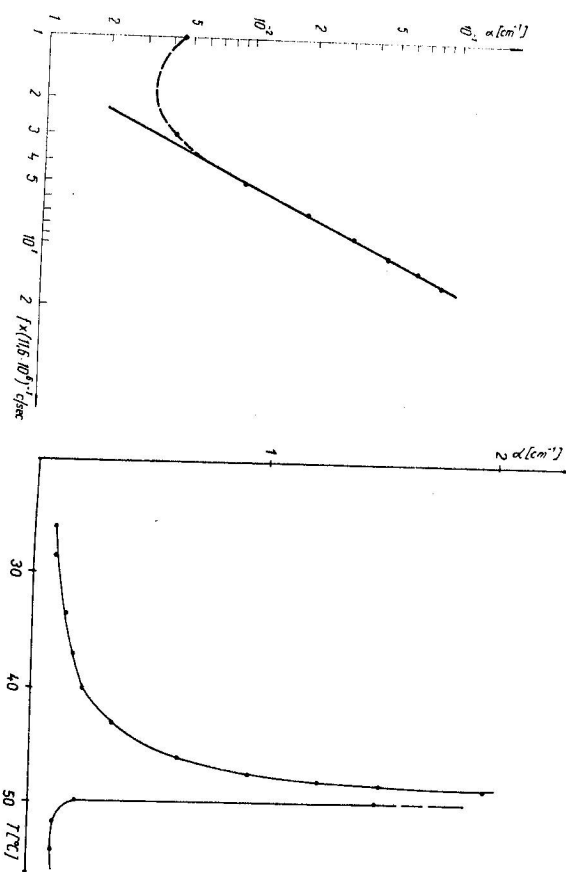


Fig. 1. The frequency dependence of attenuation of quasi-longitudinal ultrasonic waves in the Z-direction of a TGS single crystal at room temperature.

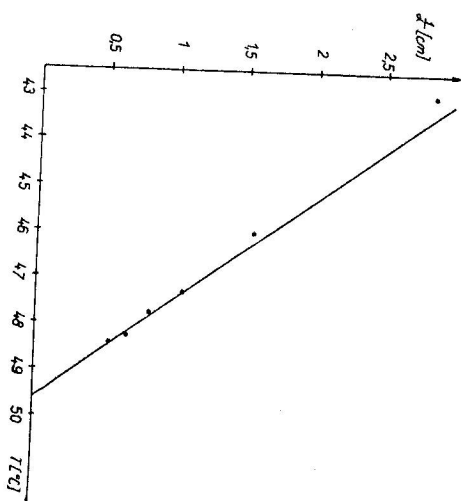


Fig. 2. The temperature dependence of attenuation of quasi-longitudinal ultrasonic waves in the Z-direction of TGS, $f = 58$ Mc/s.

Fig. 3. The dependence of α^{-1} vs. T in the vicinity of Curie temperature, $f = 58$ Mc/s.

We can see from Fig. 3 which shows the dependence of α^{-1} vs. T at $E = 0$ V/cm, that $\alpha \sim (T_c - T)^{-1}$ and we can find $T_c = 49.6^\circ\text{C}$. If we put $\alpha = 4\pi\omega^2$, from Fig. 3 $(4\pi)^{-1} = 60.63 \times 10^{15} / T$ [CGS]. The value c in relation (24) can be also computed. If we take the value P_s from (5), c becomes: $c = (8.4 \pm 0.9) \times 10^{-7} \text{ Asec}^{-5/2}$ in the vicinity of T_c . The value c seems to be temperature dependent.

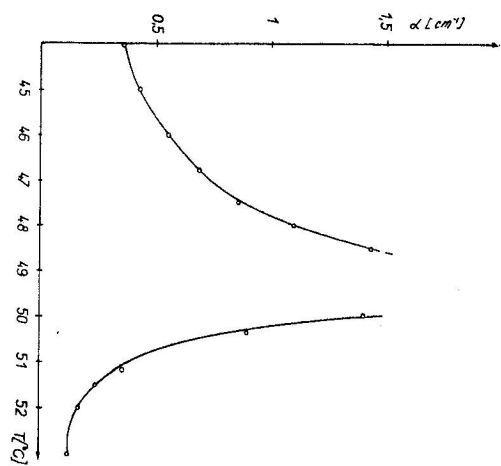
O'Brien and Litovitz [1] have found $T_c = 49.09^\circ\text{C}$ and $(4\pi)^{-1} = 20.6 \times 10^{15} / T$ [CGS]. The difference between our results and those referred into [1] is not great and it can have been caused by the difference of the samples and also by the different orientation of the latter.

Table 1

$E = 0$ V/cm	T [°C]	26	33.5	37	40	46	47.3	48.25	48.4	49.3	49.8	51.8	52
	α [cm $^{-1}$]	0.09	0.15	0.18	0.22	0.64	0.95	1.52	1.87	1.5	0.2	0.12	0.1
$E = 1$ kV/cm	T [°C]	44	45	46	46.8	47.5	48	48.5	50.05	50.2	51.5	52	53
	α [cm $^{-1}$]	0.36	0.43	0.55	0.69	0.86	1.1	1.44	1.4	0.8	0.24	0.17	0.12
$E = 3.5$ kV/cm	T [°C]	44	45	45.5	46	46.8	47.5	48	48.5	50.4	51.5	52	53
	α [cm $^{-1}$]	0.35	0.42	0.43	0.47	0.61	0.75	0.93	1.07	0.95	0.7	0.63	0.5

Figs. 4. and 5 show the dependence of α on temperature at $E = 1$ kV/cm and $E = 3.5$ kV/cm, respectively. We can see that the applied electric field changes the dependence of α on T . Unfortunately, we were not able to measure the attenuation in the vicinity of 49.5°C , since in this region the attenuation

Fig. 4. The dependence of α vs. T at $E = 1$ kV/cm, $f = 58$ Mc/s.



is too high and the used delay line decreases the amplitude of the measured echo below the sensitivity of our equipment.

The single crystal TGS is monoclinic for temperatures below and above T_c and no pure longitudinal mode can propagate in its Z-direction [8]. Because of this the quantitative comparison of the theory with experimental results causes some difficulties. In spite of it the quantitative agreement between theory and experiment was found. A more detailed experimental investigation of the ultrasonic attenuation in a single crystal of TGS under field conditions is in [9].

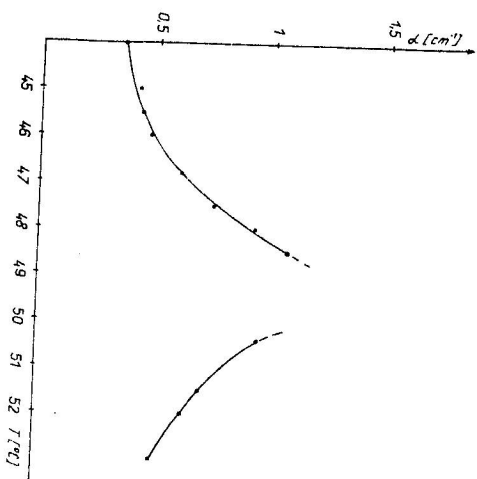


Fig. 5. The dependence of α vs. T at $E = 3.5$ kV/cm, $f = 58$ Mc/s.

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