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LOW FREQUENCY INVESTIGATION OF NONLINEAR EFFECTS IN DIELECTRICS*

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This paper presents a discussion of the possibility to investigate phonon echoes, amplification of ultrasonic waves in a high frequency electric field, and generation of a high frequency electric field through the nonlinear mixing of two ultrasonic waves at a low frequency range.

Experimental results obtained when generating a high frequency electric field by the mixing of two quasi-longitudinal ultrasonic waves propagating in the Z-direction of a ferroelectric single crystal of triglycine sulphate are reported. It is shown that a nonlinear elasto-electric coupling constant has an anomalous maximum in the vicinity of the Curie temperature.

ИССЛЕДОВАНИЕ НЕЛИНЕЙНЫХ ЭФФЕКТОВ В ДИЭЛЕКТРИКАХ ПРИ НИЗКИХ ЧАСТОТАХ

В работе обсуждается возможность исследования фононового эха, усиления ультразвуковых волн в высокочастотном электрическом поле и образование высокочастотного электрического поля с помощью нелинейного смешения двух ультразвуковых низкочастотных волн. Экспериментальные результаты получены для случая, когда исследовалось образование высокочастотного электрического поля с помощью смешивания двух квазипродольных ультразвуковых волн, распространяющихся вдоль оси сегнетоэлектрического монокристалла сульфата триглицина. Показано, что упруго-электрическая постоянная связи обладает аномальным максимумом вблизи точки Кюри.

I. INTRODUCTION

It has been shown [1, 2] that the phonon echo, the amplification of ultrasonic waves in a high (h.f.) electric field, and the generation of a h.f. electric field through the nonlinear mixing of two ultrasonic waves (u.w's) are three related effects. They appear as macroscopic manifestations of the elasto-electric nonlinearity of materials.

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All the mentioned effects are intensively studied mainly to serve the purpose of technical applications. There is, however, a very important physical reason for their investigation as they can bring unique information on the elasto-electric anharmonic properties of materials. Technical applications necessitate the knowledge of electric values on external circuits only, the physical investigation requires relations between external and internal physical values to be established.

Measurements of such physical quantities as the amplitude of u.w. and the amplitude of the h.f. electric field in the investigated sample at very high frequencies is very difficult, therefore started with the investigation of phonon echoes, the generation of the h.f. electric field by the mixing of two u.w., and the amplication of u.w. in the h.f. electric field in the low frequency region, and this paper will be devoted to this problem.

We shall discuss the possibility to study the effects at low frequencies (10^7 Hz) and we shall present some experimental results of investigation of a single domain ferroelectric crystal of Triglycine Sulphate (TGS).

II. REMARKS ON LOW FREQUENCY METHODS OF INVESTIGATION OF THE ELASTOELECTRIC NONLINEARITY OF DIELECTRIC SOLIDS

à) *Phonon echo*

The phonon echo has been discussed as the macroscopic analogy of the spin echo [3—5]. Actually, if a h.f. electric pulse is applied to a piezoelectric sample at the time 0 and another h.f. electric pulse is applied to the sample at the time τ, then at the time 2τ the sample radiates a h.f. electric pulse of angular frequency ω provided that the angular frequency of the second pulse was $2\omega/n$, where ω is the angular frequency of the first pulse and n is an integer indicating the order of the echo [6].

This effect can be phenomenologically described as follows: The first h.f. electric pulse generates through the piezoelectric surface excitation u.w. which propagate in the sample. The second pulse, besides repeating the surface excitation, generates from primary u.w's backward travelling waves. The backward travelling u.w's retrace the primary wave path and they reestablish their phase coherence at the surface just at the time 2τ and radiate through an inverse piezoelectric surface excitation h.f. electric energy. Extending this description and using the concept of phonons and photons the phonon echo and the amplification of u.w. in a h.f. electric field can be discussed as an n-photon two phonon interaction [7]. Actually, if n photons of the wave vector $\boldsymbol{\gamma}$ and the angular frequency ω_γ, which represent the h.f. electric field, annihilate under the stimulating action of u.w., which consists of phonons of the wave vector $\boldsymbol{q}$ and the angular frequency ω_q, then with a certain probability two phonons can be created. One phonon $(\boldsymbol{q}\,;\,\omega_q)$ and another phonon

$(\boldsymbol{q}^*\,;\,\omega_{q^*})$. The law of conservation of energy and quasi-momentum for the interacting quasi-particles gives:

$$n\omega_\gamma = \omega_q + \omega_{q^*}; \quad n\boldsymbol{\gamma} = \boldsymbol{q} + \boldsymbol{q}^*. \tag{1}$$

As ω_γ is in the region of ultrasonic frequencies $|\boldsymbol{\gamma}|$ is small in comparison with $|\boldsymbol{q}|$ or $|\boldsymbol{q}^*|$ so that we can put $\boldsymbol{q} = -\boldsymbol{q}^*$. Thus the phonons $(\boldsymbol{q}^*\,;\,\omega_{q^*})$ travel in the direction $-\boldsymbol{q}$ and give rise to a backward travelling phonon echo wave, while the phonons $(\boldsymbol{q}, \omega_q)$ contribute to the primary stimulating u.w. which appears as its amplification.

Relations (1) are the general conditions of the existence of the effect. These conditions in a general case can be fulfilled for three different values of ω_γ since from (1) we get $\omega_\gamma = n^{-1}\omega_q\ (1 + v_{q^*}v_q^{-1})$. Thus the u.w. $(\boldsymbol{q}, \omega_q)$ a principal phonon echo of the n^{th}-order can be obtained when we use a h.f. electric pulse of the angular frequency $\omega_\gamma = 2\omega_q n^{-1}$. Using a h.f. electric field of the angular frequency $\omega_\gamma = n^{-1}\omega_q\ (1 + v_{q^*}v_q^{-1})$, where $v_q \neq v_{q^*}$, a phonon sub-echo should be observed. The mode of the phonon sub-echo and the mode of the primary u.w. are different, while the modes of the principal phonon echo and the primary wave are the same. It should be pointed out, here, that a phonon sub-echo, of a different polarization and frequency will in general not be observable. In order that they be observable the initial forward wave must be launched from a single flat surface, whereas experiments are usually performed in rough cut samples. This is because only a backward wave of the same polarization will retrace the initial forward wave path so as to arrive at the phase at all points on the boundary of the sample.

The power of the phonon echo wave of the n-order generated from the u.w. $(\boldsymbol{q}\,;\,\omega_q)$ can be expressed in the form:

$$P_{q^*} = \frac{G_n^2 L_q^2 \omega_q^2}{2^{2+n} \varrho^2 v_q^3 v_{q^*}^3}\, P_q E_\gamma^{2n}, \tag{2}$$

where P denotes the power, L_q is the length of the interaction volume measured in the direction $\boldsymbol{q}$, ϱ is the mass density, E_γ is the amplitude of the h.g. electric pulse, and G_n is the nonlinear elasto-electric coupling constant defined by the relation

$$G_n = \frac{1}{n\,!}\, \frac{\partial^n c_{ijkl}}{\partial E_{s_1} \partial E_{s_2} \ldots \partial E_{s_n}}\, m_i^{(q)} m_k^{(q^*)} k_j^{(q)} k_l^{(q^*)} k_{s_1}^{(\gamma)} k_{s_2}^{(\gamma)} \ldots k_{s_n}^{(\gamma)}, \tag{3}$$

where c_{ijkl} are piezoelectrically stiffened elastic moduli, $m_i^{(q)}$ are the components of the unit vector $\boldsymbol{q}/q$; $k_i^{(q)}$, and $k_i^{(\gamma)}$ are the direction cosines of the polarization of the phonon $(\boldsymbol{q}\,;\,\omega_q)$, and the photon $(\boldsymbol{\gamma}, \omega_\gamma)$ respectively. Summation over the repeated lower indices i ; j ; k ; l ; s_1 ; s_2 ; … ; s_n is understood.

We can see that G_n is the $(n+4)^{\text{th}}$ rank tensor. Since odd rank tensors have zero values in the centro-symmetric point groups the echoes of odd orders can be observed only in noncentrosymmetric point groups, while echoes of even orders could be observed also in amorphous materials.

Relations (2) and (3) show that for investigating phonon echoes an exact knowledge of the direction of propagation and polarization of the interacting waves and the field is necessary together with the possibility to measure their amplitudes or powers. From this point of view the investigation of phonon echoes in the low frequency range should be convenient.

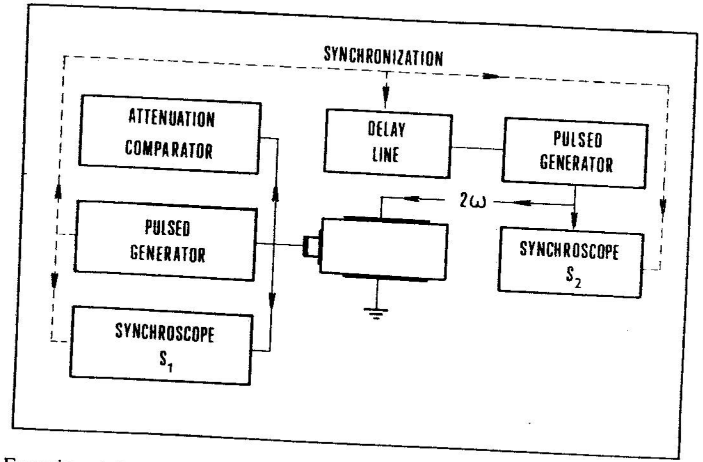

Fig. 1. Experimental arrangement for the investigation of the phonon echo at low frequencies

We shall limit our following discussion to remarks concerning the possibility of investigating the principal phonon echo of the first order at low frequencies, since the discussion can be generalized to higher orders phonon echoes and sub-echoes without difficulties.

For the purpose of investigating the phonon echo at low frequencies an experimental device sketched in Fig. 1 was suggested.

The investigated sample prepared in the form of a parallelepiped has been polished so that its end surfaces are flat and parallel. A golden electrode has been vapour deposited on the first end surface and two other electrodes have been attached to the side walls of the sample. A piezoelectric quartz transducer has been sealed to the first end surface and excited from a pulse generator by h.f. electric pulse of an angular frequency ω. A regular train of ultrasonic echoes can be observed on the screen of the synchroscope s_1 that serves as a voltmeter to measure the amplitude of the first regular ultrasonic echo. When we use attenuation comparator the coefficient of the ultrasonic attenuation can be measured too. The second h.f. electric pulse of the angular frequency 2ω is applied to the side walls electrodes at the time τ when the ultrasonic pulse passes between them. The amplitude V_2 of the second h.f. electric pulse is measured with the synchroscope S_2. The phonon echo obtained at the time 2τ through the piezoelectric transducer is measured by means of an attenuation comparator and the synchroscope S_1. Then the coupling constant G_1 can be calculated as

$$G_1 = \frac{4\varrho v^2 V_3 d}{\omega T_1 V_1 V_2} e^{-2\alpha(T-\tau)}, \tag{4}$$

where $v_q = v_{q^*} = v$ is the ultrasonic wave phase velocity, V_1 is the amplitude of the voltage of the first regular ultrasonic echo, V_2 is the amplitude of the second h.f. electric pulse, V_3 is the amplitude of voltage of the phonon echo, T_1 is the duration time of the first pulse, d is the distance of the side walls electrodes, α is the attenuation coefficient expressing the decrease of amplitude of the u.w. with time, and $T = L/v$ is the time during which the u.w. travels through the sample of length L.

In most cases the first h.f. pulse of an amplitude of the order 10^3 V gives the first ultrasonic echo of an amplitude of the order 10 V so that the phonon echo whose amplitude corresponds to the voltage 10^{-5} V can be observed when we use standard technique provided that the length of the sample is sufficiently long to produce regular ultrasonic echoes well distinguishable from the phonon echo.

Taking the typical values $\varrho = 2 \times 10^3$ kg m^{-3}, $v = 4 \times 10^3$ ms^{-1}, $\omega = 10^8$ Hz, $T_1 = 10^{-5}$ s and $d = 10^{-2}$ m in relation (4) one can show that phonon echoes in materials having $G_1 = 10^{-3}$ N/Vm should be observable. This is a quite good sensitivity since G_1 in LiNbO$_3$ is of the order 10 N/Vm [2].

b) Amplification of ultrasonic waves in a high frequency electric field

As we already know the n annihilating photons (γ, ω_γ) create under the stimulating action of the phonons $(\boldsymbol{q}, \omega_q)$ the phonon $(\boldsymbol{q}, \omega_q)$ and the phonon $(\boldsymbol{q}^*, \omega_{q^*})$. While the phonons $(\boldsymbol{q}^*, \omega_{q^*})$ create a backward travelling wave the phonons $(\boldsymbol{q}, \omega_q)$ contribute to the stimulating wave which appears as its amplification.

The power of the stimulating u.w. can be expressed in the form:

$$P_q(x) = P_q(0) \exp\left[-\left(2\alpha' - \frac{G_n^2 E_\gamma^{2n} \omega_q \omega_{q^*}}{2^{2n+2} \varrho^2 v_q^3 v_{q^*}^3} x\right) x\right], \tag{5}$$

where α' expresses the decrease of amplitude of the u.w. per unit length and x is the interaction length.

Analyzing relation (5) we can see that the total attenuation coefficient depends on the interaction length and it becomes negative for $x > x_0 = [(32\varrho^2 v^6 / G_1^2 E_\gamma^2 \omega^2)\alpha']$ when we use the experimental arrangement shown in Fig. 2, where the pulsed generator excites through a piezoelectric transducer ultrasonic pulses in the sample and a c.w. generator gives a continuous h.f. electric field across the side walls electrodes, an echo train decreasing up to the distance x_0 should be observed. Then for echoes correspondig to $x > x_0$ an amplification of the ultrasonic pulse should be obtained.

Here we should mention that all the above formulae are valid under the assumption that the initial state of the wave generated through the nonlinear interaction is empty. Thus amplification can be observed only in the case when the amplitude of the phonon echo wave does not reach the noise-level before it reaches the distance x_0. If the amplitude of the phonon echo wave is comparable with the amplitude of thermal phonons, a strong back-scattering takes place and the amplifying effect is not observed.

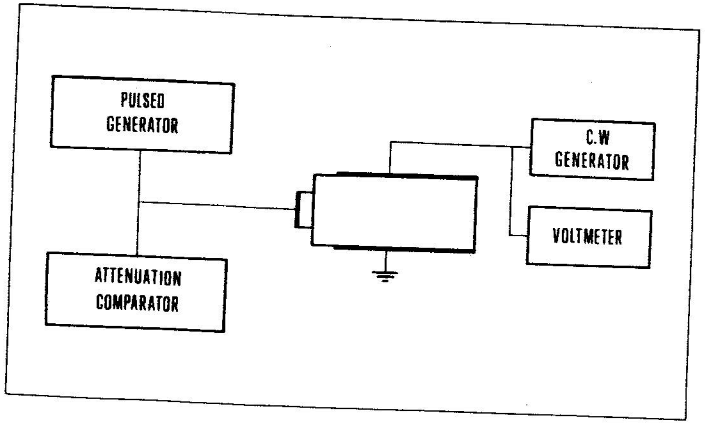

Fig. 2. Experimental arrangement for the investigation of the amplification of ultrasonic waves in a high frequency electric field

c) Generation of a high frequency electric field by mixing of two ultrasonic waves

We can describe the generation of a h.f. electric field by the mixing of two u.w. using a process whereby two annihilating phonons ($\mathbf{q}_1; \omega_1$) and ($\mathbf{q}_2, \omega_2$) create a phonon (γ, ω_γ).

The average power of the generated h.f. electric field can be expressed as:

$$P_\gamma = \frac{V^2}{32\pi} \frac{G^2 \omega_\gamma^4 \omega_1^2 \omega_2^2}{v_1^2 v_2^2 \varepsilon_\gamma c_\gamma^3} A_{01}^2 A_{02}^2, \tag{6}$$

where V is the interaction volume, $\varepsilon_\gamma = \sum_{i,j} k_i^{(\gamma)} \varepsilon_{ij} k_j^{(\gamma)}$ is the effective dielectric constant, c_γ is the velocity of light in the investigated medium, A_0 is the amplitude of the corresponding u.w. and the average nonlinear elasto-electric coupling constant G^2 is given as:

$$G^2 = \frac{1}{3} \sum_i \left(\sum_{klmn} \frac{\partial c_{klmn}}{\partial E_i} m_k^{(q_1)} m_m^{(q_2)} k_l^{(q_1)} k_n^{(q_2)} \right)^2. \tag{7}$$

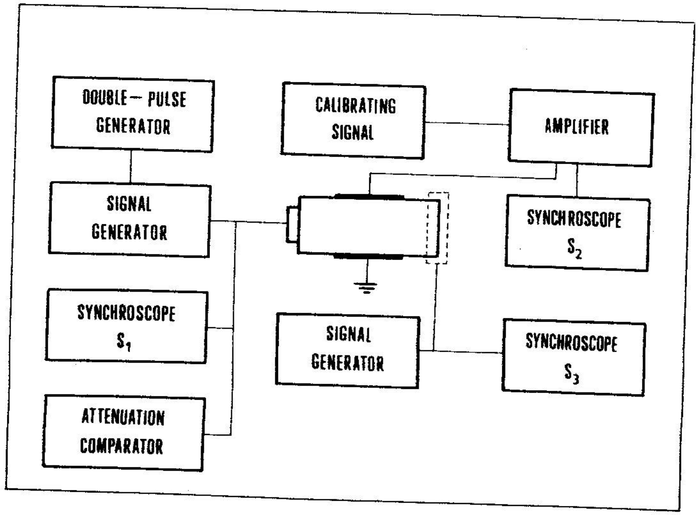

Fig. 3. Experimental arrangement for the investigation of the generation of a high frequency electric field by nonlinear mixing of two ultrasonic waves travelling in opposite directions

The low frequency experimental arrangement for the investigation of this effect is schematically shown in Fig. 3.

A double pulse generator is used to switch on the signal generator that generates two h.f. electric pulses. The first at the time 0 and the second at the time τ. Both h.f. electric pulses excite the piezoelectric transducer. The time τ is chosen so that the ultrasonic pulse generated by the second h.f. electric pulse meets the first ultrasonic pulse after its reflection from the second end surface in the middle of the sample. These two ultrasonic pulses travelling in opposite directions generate the 2ω electric pulse that can be observed through the amplifier on the screen of the synchroscope S_2.

The nonlinear coupling constant G, the power P_γ of the h.f. electric field together with the amplitude of u.w. should be measured. The measurement of power requires a careful analysing of the investigated process. This analysis yields an equivalent scheme shown in Fig. 4, where C_0 is the capacity of the side walls electrodes, R is the external load, R_i represents the internal losses of the h.f. energy in the sample, and u is the alterning voltage source corresponding to the internal electric field generated through nonlinear interaction. Assuming that R and R_i are real and $R \gg R_i$, then practically the total power P_Y of the alternating voltage source is scattered through the resistor R. Thus fulfilling the condition $R \gg R_i$, the average power P_Y generated in space between the side walls electrodes can be measured on the external load.

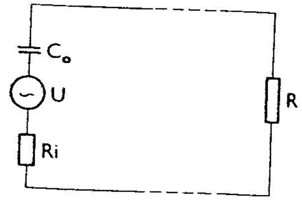

Fig. 4. Equivalent scheme of a high frequency electric field generator created by two nonlinearly mixed ultrasonic waves in a dielectric sample

Simultaneously with the measurement of the power P_Y the measurement of amplitudes of the interacting u.w. is necessary. In order to measure the amplitudes of the u.w., the piezoelectric surface excitation of the second end surface of the sample is used.

Preparing this part of experiment calculation of optimum direction of external electric field exciting required ultrasonic mode should be done using procedure described in [8].

First we choose the right-handed coordinate system $(x_\alpha, x_\beta, x_\gamma)$ so that the x_α axis is perpendicular to the surface of the sample and x_β, and x_γ are on the surface oriented so that the transformation of all the tensor properties of the investigated sample from an ordinary crystallographic system to the system $(x_\alpha, x_\beta, x_\gamma)$ is as simple as possible. Then the optimum direction of the external electric field $E_0^{(ex)}$ for the excitation of the u.w. (q_1, ω_1) is given by the direction cosines n_i, where

$$n_i = \sum_j \frac{k_j^{(q_1)} e_{ij\alpha}}{|e^{(e)}|} \tag{8}$$

where j runs over α, β, γ, and the components $e^{(e)}$ are given as

$$e_i^{(e)} = \sum_j k_j^{(q_1)} e^*_{ij\alpha}, \tag{9}$$

while the modified piezoelectric constants e^*_{ijk} are given as

$$e^*_{\alpha j\alpha} = e_{\alpha j\alpha}\varepsilon_0/\varepsilon^s_{\alpha\alpha} \tag{10}$$

and

$$e^*_{ij\alpha} = e_{ij\alpha} - e_{\alpha j\alpha}\varepsilon^s_{i\alpha}/\varepsilon^s_{\alpha\alpha}; \quad i \neq \alpha,$$

where ε^s_{ij} are the components of the dielectric constants tensor at a constant strain.

In most practical cases we meet two different situations.

1) The optimum direction $\boldsymbol{n}$ is parallel to the excited surface. In this case the electrodes for the application of the external electric field are attached to the surface in a way shown in Fig. 5(a). Applying a h.f. electric field of the strength V_s/d_e, an u.w. of the amplitude

$$u_0 = \frac{|e^{(e)}|}{\varrho v_1 \omega_1} \frac{V_s}{d_e} \tag{11}$$

— where d_e is the width of the gap between the electrodes and V_s is the amplitude of the applied voltage — is generated.

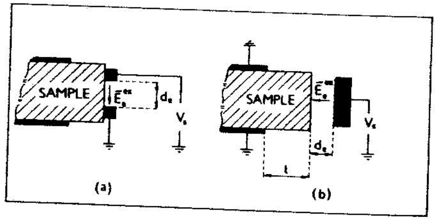

Fig. 5. Arrangement of electrodes for piezoelectric surface excitation of ultrasonic waves; (a) the external electric field is parallel to the excited surface; (b) the external electric field is perpendicular to the excited surface

2) The optimum direction is perpendicular to the excited surface. In this case a piston electrode parallel to the surface is placed above the surface in a way shown in Fig. 5(b). If the width of the gap between the excited surface and the electrode is $10L/\varepsilon_r$, where ε_r is relative dielectric constant measured in direction perpendicular to the surface, then with an accuracy better than 5 % the amplitude of the voltage V_s divided by d_e gives the amplitude of the external exciting field strength, and the formula (11) holds also in this case.

The ultrasonic pulse of the required frequency and the polarization excited at the second end surface propagate in the sample and can be received by a quartz transducer at the first end surface. Since the amplitude of an u.w. generated at the second end surface can be calculated by formula (11), the relation between the amplitude of the voltage of the transducer and the amplitude of the u.w. reflected from the first end surface can be easily established. Having this relation, the amplitudes of the u.w. used in the nonlinear generation of the h.f. electric field can be estimated.

When we use a standard experimental technique through an u.w. of an amplitude of the order 10^{-11} m can be generated piezoelectric surface excitation. This u.w. is sufficient to calibrate the quartz transducer. The quartz transducer can generate u.w.'s of an amplitude of the order 10^{-9} m, which makes it possible to investigate the generation of a h.f. electric field in materials having the value G of the order 10^{-3} N/Vm.

III. EXPERIMENTAL RESULTS AND CONCLUSIONS

Using the procedure described in the previous section, the generation of a h.f. electric field by a nonlinear mixing of two quasi-longitudinal ultrasonic waves propagating in the Z-direction of a single domain ferroelectric single crystal of Triglycine Sulphate (TGS) has been investigated in the temperature region from 293 K to 324 K.

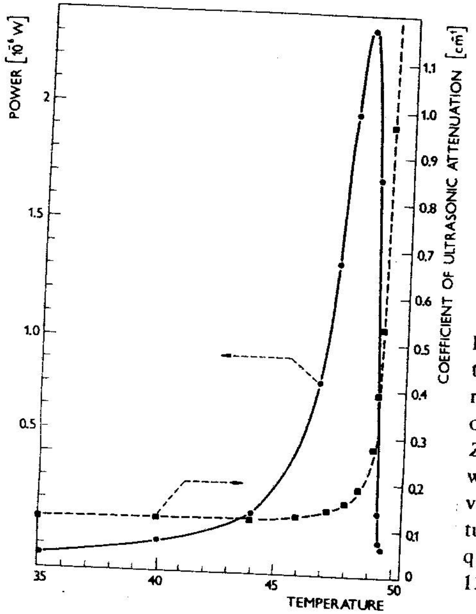

Fig. 6. Temperature dependence of the power of the electric field of the frequency 27.6 MHz generated by two quasi-longitudinal ultrasonic waves of the frequency 13.8 MHz propagating in the Z-direction of TGS. Amplitudes of ultrasonic waves at room temperatures 293.9 K have the value 28.3×10^{-10} m, (full line) and the temperature dependence of the attenuation coefficient of quasi-longitudinal ultrasonic waves of frequency 13.8 MHz propagating in the Z-direction in TGS (dashed line)

The sample of TGS had dimensions $L_x = 0.8$ cm, $L_y = 0.92$ cm, and $L_z = 1.21$ cm, where L denotes the length of the edge of the sample in the crystallographic direction indicated by the subscript. The width of the side walls electrodes in the middle of the Y-surface of the sample was 0.3 cm. An RLC circuit tuned to its resonance frequency at 27.7 MHz served as an impedance transformer with an equivalent resistance 685 Ω and it was connected to the side walls electrodes to receive the h.f. electric signal generated in the sample by the u.w. of a frequency 13.8 MHz.

Results of measurements are presented in Fig. 6. The full line in Fig. 6 is passed through experimental points obtained when the average power of the 27.6 MHz electric field generated by two quasi-longitudinal u.w. propagating in the Z-direction in TGS and having the frequency 13.8 MHz has been investigated as a function of temperature. Both u.w. at the first end surface of the sample had initially the amplitude 28.3×10^{-10} m and they generated an electric field of the power 4×10^{-9} W at a temperature 293.9 K.

Simultaneously with the measurement of the power the temperature dependence of the attenuation coefficient of quasi-longitudinal u.w. of the frequency 13.8 MHz propagating in the Z-direction of TGS has been measured. Results of this measurement are in Fig. 6, dashed line.

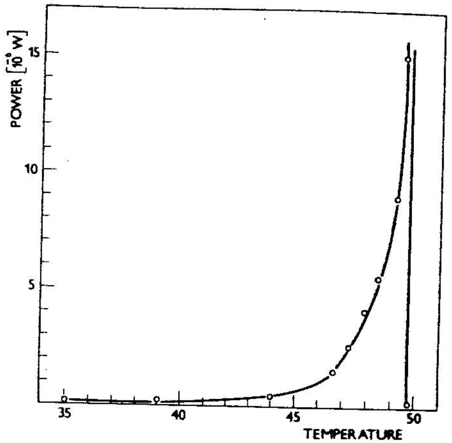

Fig. 7. Temperature dependence at the power of a 27.6 MHz electric field generated by two ultrasonic waves of the frequency 13.8 MHz and the amplitude 28.3×10^{-10} m and propagating in the Z-direction in TGS

Results in Fig. 6 show that the power of the h.f. electric field increases with increasing temperature up to 321.66 K. The following decrease of the generated power above 321.66 K is due to an increasing ultrasonic attenuation which has a maximum at 322.76 K.

Fig. 7 shows the power of the h.f. electric field if generated by a u.w. of a constant amplitude of 28.3×10^{-10} m.

Our results show that a TGS crystal has a relatively large value of the nonlinear elasto-electric constant. The room temperature (293.9 K) value of the average nonlinear elasto-electric constant is $G = 400$ N/Vm. This constant depends on temperature and it exhibits an anomalous maximum in the vicinity of the Curie point 322.76 K. The anomalous maximum of the constant G at the Curie temperature is a consequence of the fact that the elastic properties of TGS in the vicinity of the phase transition strongly depend on the external electric field.

The accuracy of measurements of the relative change of the generated power with temperature was better than 5 %, however, the accuracy in the evaluation of the constant G was due to an inaccuracy in the estimation of the interaction volume and an inaccuracy in the estimation of the amplitude of the u.w. very poor. Therefore the value $G = 400$ N/Vm can be considered as an estimation of the order only.

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