Polarization echo near ferroelectric phase transitions

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(Submitted 19 May 1981)
Zh. Eksp. Teor. Fiz. **81**, 2111–2117 (December 1981)

The polarization echo and pulsed polarization switching methods were used to study the electroacoustic interaction at temperatures near the Curie points of uniaxial ferroelectric crystals of Rochelle salt and KDP in the ultrasonic frequency range. The investigated electroacoustic echo and convolution signals were due to the contribution of the domain polarization switching to electroelasticity. The polarization echo method was used to obtain ultrasonic data under conditions of critical scattering and dispersion of sound, and also for technical realization of the extremal nonlinearity of the crystals near phase transitions.

PACS numbers: 77.80.Dj, 72.50. + b, 43.35.Qv

1. INTRODUCTION

A characteristic instability of the crystal lattice in the region of structural phase transitions makes it possible to modulate the elastic properties of crystals by relatively weak external fields of different physical origins. Modulation of the elasticity can sometimes result in the interaction of an acoustic field in a crystal with an external pump field.

If the crystal symmetry is such that there are nonzero coefficients of the electroelastic coupling η in the expansion of the free energy of a crystal

$$F={}^1/_2c_{ijkl}S_{ij}S_{kl}+\eta_{ijklm}S_{ij}S_{kl}E_m+\ldots, \quad (1)$$

where c is the elasticity tensor of the crystal, S is the strain tensor, and E is the electric field, then in the case of a nonlinear crystal there is an interaction between elastic and electromagnetic waves[1-3] whose frequencies and wave vectors satisfy the laws of conservation of energy and momentum $\mathbf{k}_1+\mathbf{k}_2=\mathbf{k}_3$ and $\omega_1+\omega_2=\omega_3$, where $\omega_1, \mathbf{k}_1$, $\omega_2, \mathbf{k}_2$ are the frequencies and wave vectors of the elastic waves and $\omega_3, \mathbf{k}_3$ are the corresponding parameters of the electromagnetic waves.

We shall report an experimental investigation of an electroacoustic interaction of this kind in the radiofrequency (rf) range (~10^7 Hz) at temperatures near the ferroelectric phase transition points T_c of uniaxial ferroelectric crystals of Rochelle salt and KDP (Refs. 4 and 5). An effective electroacoustic interaction near phase transitions in these crystals makes it possible to observe: a) a signal due to a polarization electroacoustic echo in the form of a traveling acoustic wave with a wave vector reciprocal in relation to the primary acoustic wave when this wave interacts with a pulse of an alternating electric field distributed homogeneously throughout the crystal; b) a convolution signal in the form of a pulse of an alternating electric field when two opposite acoustic waves interact in a crystal.

2. EXPERIMENTAL METHOD

We investigated samples of Rochelle salt (T_c = 24.2 °C) and KDP (T_c = −151.2 °C), which were optically transparent and uncolored. A crystal in the form of a slab of 1–2 cm^3 volume and ~0.5 cm thickness had foil-coated surfaces perpendicular to the polar axis and was placed inside a capacitor which was thermostatted to within 0.01 °C (Ref. 6) and connected to an oscillatory circuit with two resonance frequencies $\omega/2\pi$ amounting to 12 and 24 MHz. The two foil-coated surfaces were used to apply a homogeneous alternating electric field $\mathbf{E}_\sim$ (in the form of rf or video pulses) and a static bias field $\mathbf{E}_0 \parallel \mathbf{E}_\sim$. An echo signal at a moment 2τ and a convolution signal at a moment $\tau+\tau_1/2$ (Fig. 1) appeared only when the electric field was parallel to the polar axis and was applied in the form of rf pulses of amplitudes E_1, E_2, and E_3 in a sequence and with frequencies shown in Fig. 1; the elastic waves participating in the interaction had different velocities and frequencies $\omega_1=\omega_2=\omega$, whereas the electric pump field homogeneous throughout the crystal ($k_3=0$) had the frequency $\omega_3=2\omega$. The elastic wave (ω_1, k_1) was excited either with a Y-cut quartz transducer emitting a transverse wave along the z direction representing one of the nonpolar axes of the crystal with the polarization perpendicular to the polar axis or due to piezoelectric properties of the crystal when an electric pulse of carrier frequency ω was applied to the capacitor probe electrodes.

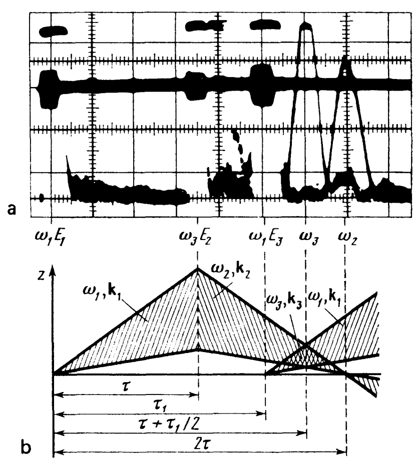

FIG. 1. a) Oscillogram of the polarization echo and convolution signals obtained for KDP at T = −149°C (sweep rate 20 μsec/cm, E_0 = 3.37 kV/cm, $E_1=E_3$ = 0.45 kV/cm, E_2 = 0.3 kV/cm). b) Diagram showing the scattering of acoustic pulses along the direction of propagation of z corresponding to the oscillogram in Fig. 1a.

 0038-5646/81/121122-04$02.40

The nature of the investigated signals was identified by developing the following method for determining the electroelastic properties in the process of polarization reversal in ferroelectric crystals subjected to pulsed electric fields.

The investigated crystals were of size z_0 between the plane-parallel faces normal to the z direction and they were subjected along the polar axis to a field $E_{\sim}$ in the form of alternate bipolar video pulses each with a leading edge ≤ 20 nsec and duration ≥ 50 μsec, and to a static field E_0. Each of the bipolar electric field pulses generated polarization switching current pulses accompanied by the current of free piezoelectric resonance vibrations at a frequency corresponding to the effective elastic modulus and the size z_0 of the crystal. The currents were recorded by connecting a $R = 200\ \Omega$ resistor in series with the capacitor electrodes. These bipolar pulses were used to excite, as in the polarization echo method, acoustic vibrations interacting with the electric polarization along the polar axis, characterized by critical attenuation and scattering on domains in the phase transition region.[7] In contrast to the echo method the piezoelectric resonance vibrations of the crystal excited by the leading edge of a video pulse appeared against the background of a strong electric field pulse and a strong coercive force, i.e., under conditions of a strong reduction (by the electric field) in the polarization relaxation time and a corresponding reduction in the acoustic losses.[8] Consequently, such piezoelectric resonance vibrations showed no significant anomalies of the acoustic losses near T_c, which made them suitable for determining the changes in the effective velocity of sound when a domain system in a crystal was subjected to a polarization switching pulsed electric field $E_{\sim}$, increasing temperature, and bias static field E_0. Measurements of the period of the piezoelectric resonance vibrations yielded the coefficient of modulation of the effective velocity of sound by an electric field $E_{\sim}$ in accordance with the formula

$$A_v = |\tau_+ - \tau_-| / (\tau_+ + \tau_-),$$

where τ_+ and τ_- are the periods of free vibrations excited by the positive and negative video pulses, respectively.

The method of pulsed polarization switching can find more general applications in investigations of electroelastic (magnetoelastic) properties of crystals, which need not be ferroelectric. The sensitivity of the method can be increased significantly by monitoring the change in the large number of periods τ of free resonance vibrations.

3. EXPERIMENTAL RESULTS

1. The echo and convolution signals were observed for Rochelle salt in the temperature range from +30 to −27 °C ($E_0 = 0.5$ kV/cm) and near the Curie points +24.2 °C and −18 °C the signal amplitudes were maximal; in the case of KDP these signals were observed in the vicinity of the Curie point from −151 to −147.2 °C ($E_0 = 5$ kV/cm). An increase in E_0 broadened the temperature range in which the echo signal was observed.

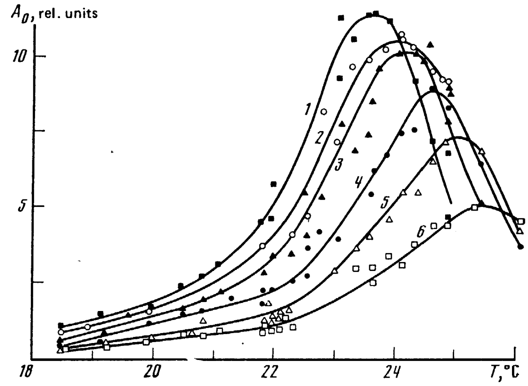

FIG. 2. Temperature dependences of the initial amplitude A_0 of the echo signals measured for Rochelle salt using fields $E_1 = E_2 = 0.2$ kV/cm and different values of E_0 (kV/cm): 1) 0.3; 2) 0.4; 3) 0.6; 4) 0.8; 5) 1.0; 6) 1.5.

The ratio of the amplitudes of the echo and convolution signals to the piezoelectric induction accompanying the pulses increased on going to the ferroelectric phase.

2. When the interval τ between the pulses E_1 and E_2 was altered, the amplitude of the echo at a moment 2τ decreased approximately exponentially $A_e = A_0 \exp(-2\tau/T_2)$. Figure 2 shows the dependence of the echo amplitude A_0 (for $\tau = 0$) on the temperature and field E_0 in the region of phase transition in Rochelle salt. The values of A_0 and T_2 were found from the dependence $A_e = f(\tau)$ recorded for each experimental point.

3. The reciprocal echo lifetime $\alpha_t = 1/T_2$Hn sec^{-1}, comparable with the sound attenuation coefficient, depended on the temperature of the sample and on the field E_0. When E_0 was increased, the value of α_t decreased, particularly on approach to the transition temperature T_c. Figure 3 shows the dependences of the attenuation coefficient of sound on the field and temperature in the vicinity of a phase transition in Rochelle salt (z is the direction of propagation of sound, $\alpha_s = 2.7\alpha_t/v_s$ cm^{-1}, where $v_s = 1.32 \times 10^5$ cm/sec is the velocity of sound).

4. The width of the echo was governed completely by

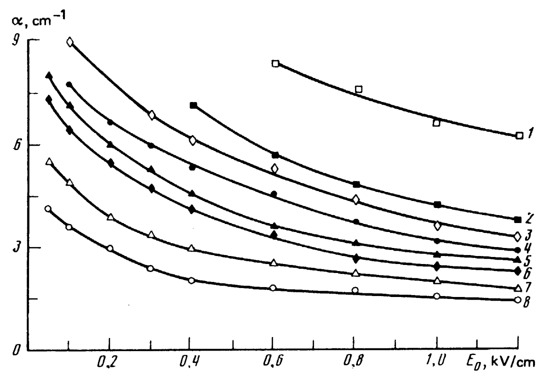

FIG. 3. Dependences of the attenuation coefficient of the transverse sound on the bias field E_0 in the critical region, measured by the echo method for $E_1 = E_2 = 0.2$ kV/cm and different temperatures near T_c of Rochelle salt (°C): 1) 25.3; 2) 24.1; 3) 23.8; 4) 23.6; 5) 23.1; 6) 22.5; 7) 20.8; 8) 18.5.

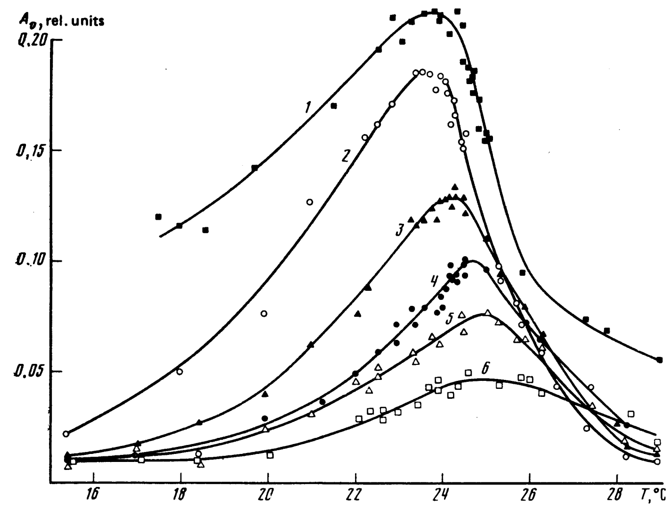

FIG. 4. Temperature dependences of the electroelasticity coefficient A_v measured for Rochelle salt using bipolar pulses of different amplitudes, $E_{\sim} = 0.7$ kV/cm, and different electric bias fields E_0 (kV/cm); 1) 0.3; 2) 0.4; 3) 0.6; 4) 0.8; 5) 1.0; 6) 1.5.

the durations of the first and second pulses Δt_1 and Δt_2, and the echo width at the base was $\Delta t_1 + 2\Delta t_2$. The dependences of the echo and convolution amplitudes on the amplitudes of each of the exciting pulses was close to linear.

5. Figure 4 shows the dependences of the electroelasticity coefficient A_v on the temperature and on the field E_0 in the region of a phase transition in Rochelle salt, as recorded by the method of polarization switching due to the application of bipolar pulses.

4. DISCUSSION

Equation (1) can be written in the form of the dependence of the effective velocity of sound on the electric pump field (the tensor indices are omitted):

$$V = V_0(1 + \eta E_{\sim}/2c + \ldots). \tag{2}$$

The modulation coefficient of the velocity of sound V by the electric field $A_v = \partial V/\partial E_{\sim}$ represents the electroelasticity, and the dependences of A_v on E_0 and temperature can obviously be compared with the corresponding dependences of the echo amplitude.

The value of A_v was determined independently of the echo method by determining the state of a crystal not from the electric but from the mechanical point of view (directly from the velocity of sound), which is an approach implied in the well-known method of bipolar pulses[9] but not hitherto utilized. The dependence of the electroelasticity coefficient A_v on the temperature and on the field E_0 (Fig. 4) is similar to the behavior of the permittivity in the region of phase transitions[10] and to the dependences on E_0 and on the temperature indicated by our measurements of the amplitude of the polarization switching current. These observations demonstrate a strong coupling between the dielectric and the electroelastic properties of the investigated crystals, which is explained by the domain contribution.

The clear correspondence between the temperature and field dependences of the echo signals (Fig. 2) with the behavior of A_v (Fig. 4) can be regarded as demonstrating the dominant contribution of the domain electroelastic nonlinearity to the intensities of the investigated echo and convolution effects. If a sensitive detector is used, the range of observation of the echo signals is wider than the range of values of A_v, indicating a high sensitivity of the echo method to the electroelastic nonlinearity.

Rochelle salt has a low value of T_2 near T_c and in weak fields E_0 the echo signal is difficult to observe because of the finite recovery time of the detector sensitivity.

The scattering by domains has prevented earlier acquisition of ultrasonic data for waves strongly coupled to the electric polarization parallel to the polar axis of a ferroelectric in the region of phase transitions occuring in large single-domain crystals.[7,11-13] These data are of interest for the dynamics of phase transitions and can be obtained by the polarization electroacoustic echo method. Figure 1(b) demonstrates the evolution of the front of an acoustic packet traveling in the bulk of a crystal along the z direction. The primary acoustic wave ($\omega_1, \mathbf{k}_1$) "diverges" at inhomogeneities in a crystal and the reverse wave ($\omega_2, \mathbf{k}_2$) created in the crystal by the wave front of the primary wave in the presence of an electromagnetic pump pulse ($\omega_3, \mathbf{k}_3$) converges at the same inhomogeneities and restores the initial front existing up to the time 2τ. A near-exponential dependence of the echo amplitude on the interval τ between the E_1 and E_2 pulses demonstrates an effective recovery of the initial front of the acoustic wave. This is supported by the appearance of the convolution signal (Fig. 1). The opposite acoustic signals ($\omega_2, \mathbf{k}_2$) and ($\omega_1, \mathbf{k}_1$), each with irregular leading edges due to the scattering and dispersion of acoustic waves by inhomogeneities of the medium, interact no less effectively and create a convolution signal ($\omega_3, \mathbf{k}_3 = 0$) at a moment $\tau + \tau_1/2$. This echo method can ensure the conditions under which a "convergent" wave ($\omega_2, \mathbf{k}_2$) has the same front configuration as a "divergent" wave ($\omega_1, \mathbf{k}_1$) at the moment when the two wave packets meet in the bulk of a crystal.

Figure 3 shows the dependences of the attenuation coefficient of sound (estimated as $1/T_2$) on the field E_0 and on the temperature. These data represent not small single-domain crystals but large polydomain crystals because of the use of the echo method. The results can be compared with the theoretical data for the ranges of phase transitions in single-domain uniaxial ferroelectrics.[8] The behavior of α_s (Fig. 3) agrees with the theoretical dependence of the attenuation coefficient of sound on the static electric field and on the temperature. As we move away from the Curie point, the influence of the field E_0 decreases and in high fields the dependence of the absorption on E_0 and on the temperature is very weak. The absence of data on α_s near the Curie points T_c at low values of E_0 is explained by the fact that under these conditions the time constant T_2 is less than the instrumental time representing the recovery of the detector sensitivity. The dependences of the amplitude and duration of the echo on the amplitudes and duration of the exciting pulses (Sec. 3.4) corresponds to the function of the echo profile in the form of the correlation integral.[1] The dependence of the convolution amplitude on the amplitudes of the exciting pulses is linear, as deduced from the function of the profile in the form of the convolution integral.[1] The duration of the convolution signal depends on the duration of the excitation pulses and on the time interval $2\tau - \tau_1$, due to the scattering of sound in the medium [Fig. 1(b)].

5. CONCLUSIONS

1. The amplitude of the polarization echo near phase transitions was found to be proportional to the electroelastic nonlinearity coefficient of the investigated crystals. The temperature and field dependences of the echo signal were described well by the contribution of the domain polarization switching to the electroelasticity of ferroelectrics in the investigated range of frequencies.

2. The polarization echo method separates the contributions of the interference (reversible) and energy (irreversible) attenuation of sound near phase transitions, and can have interesting applications for the ultrasonic probing of phase transitions in real polydomain crystals.

3. The polarization echo method ensures the interaction of acoustic waves under the conditions of critical scattering and dispersion, which should make possible technical applications (in convolution and correlation devices) of the extremal nonlinearities of the investigated crystals near their phase transitions.

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Translated by A. Tybulewicz