Anomalous generation and conversion of acoustic modes near phase transitions in ferroelectric single crystals

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A nonlinear generation of sound (at half the frequency of the pulsed rf excitation and also at twice this frequency) has been observed in Rochelle salt and KDP single crystals near the ferroelectric phase transition. This generation occurs above a threshold. A manifestation of this anomalous generation and of a conversion of acoustic modes into polarization echo signals has been demonstrated. © *1995 American Institute of Physics.*

At one time it was believed impossible to carry out pulsed ultrasonic probing of condensed media near phase transitions, because of the dispersion and scattering of sound waves by irregularities.[1] However, studies of this type were carried out successfully[2,3] after the observation of a polarization echo near the phase transition in ferroelectric Rs (Rochelle salt) and KDP (potassium dihydrophosphate) single crystals. Minima of the sound absorption in the frequency range 2–50 MHz were later observed[4] in narrower temperature intervals near the same phase transitions. The depth of these minima increased with increasing amplitude of the sound wave. Both phenomena were interpreted[5,6] as manifestations of nonlinear electroelastic properties of the single crystal near a phase transition.

In this letter we are reporting observation of a generation of sound at the frequency $\omega/2$ (half the excitation frequency ω) near a phase transition. This generation exhibits characteristic properties of the dynamic behavior of nonlinear systems.[7,8] We show that this anomalous generation and the conversion of acoustic modes can explain the mechanism for the formation of the anomalous polarization echo signal.

The experimental procedure was like that used in Refs. 2–4 and 9 to excite polarization echo signals in ferroelectric single crystals. In contrast with those previous studies, we also studied the induction signals after each train of rf exciting pulses. The reason for the interest in the behavior of the induction was the unusual behavior of the "ringing" after one rf exciting pulse. In addition to the customary induction, at the excitation frequency ω, we observed induction signals at the frequencies 2ω (the second harmonic) and $\omega/2$. Figure 1 is a typical oscilloscope trace of the induction signal $I_{\omega/2}$ at the half-frequency, $\omega/2$, after one rf pulse with a carrier frequency ω.

Here are some qualitative features of this signal.

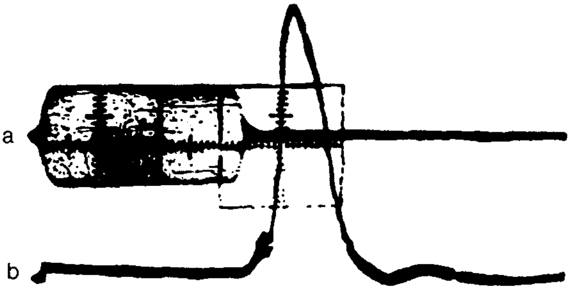

FIG. 1. Oscilloscope trace of the generation of sound at half the frequency of the exciting rf pulse. a—Radio-frequency pulse at 24 MHz; b—signal at 12 MHz (receiver operating at the end of the rf pulse). Rochelle salt single crystal, sweep time of 2 μs/cm, $T=23.7°\mathrm{C}$, $E_1=0.8$, $E_0=0.6$ kV/cm.

(1) The $I_{\omega/2}$ signal is generated above a certain threshold height of the exciting rf pulse. As the power of the rf pulse is raised above the threshold, the amplitude of the $I_{\omega/2}$ signal increases in a nonlinear fashion.

(2) The $I_{\omega/2}$ signal is generated near the phase transition in a temperature interval narrower than that (ΔT_{PE}) in which the polarization echo signals are observed.[2,3] In a Rochelle salt single crystal, for example, ΔT_{PE} is from -28 to $+32°\mathrm{C}$, while $\Delta T_{\omega/2}$ at the upper Curie point is from $+23.7$ to $+24.3°\mathrm{C}$. In KDP, ΔT_{PE} is from -160 to $-149°\mathrm{C}$, in comparison with $\Delta T_{\omega/2}$, which is from -153.3 to $-152.9°\mathrm{C}$. The intervals $\Delta T_{\omega/2}$ increase with increasing height of the rf pulse. The largest intervals $\Delta T_{\omega/2}$ which were observed were cited above.

(3) The $I_{\omega/2}$ signal coincides with the time $T_2^*(\omega/2)$, which is longer than the decay time $[T_2^*(\omega)]$ of the I_ω signal, at the excitation frequency. This situation corresponds to a relative contraction of the spectrum of the excited acoustic signal. The situation is illustrated by the noisier decay of the I_ω signals after the rf pulses in Fig. 2a (noisier in comparison with $I_{\omega/2}$ in Fig. 1). At a qualitative level, this behavior of the $I_{\omega/2}$ signal corresponds well to the threshold required for its excitation.

The generation of the second harmonic (2ω) in Fig. 2b also occurs above a threshold amplitude of the exciting rf pulse.

These properties of the anomalous sound generation near the phase transition in ferroelectric are also seen in the polarization echo signal.

Let us examine manifestations of this generation in the particular case of the excitation of the anomalous polarization echo signal at the frequency 2ω by a series of three rf pulses (Fig. 2b) with frequencies of ω, 2ω, and ω, respectively. Here are some qualitative features of the signals observed here.

(1) Each rf pulse is followed by an $I_{2\omega}$ induction signal.

(2) The anomalous echo signal at the frequency 2ω is observed at the time $\tau_e=(3/4)\times(\tau+\tau_1)$, where τ is the time at which the second pulse begins, τ_1 is a time at which the third pulse begins, and the origin for the time scale is the beginning of the first pulse. This signal is observed in a narrow temperature interval near the phase

transition. The actual interval depends on the intensities of the exciting rf pulses. The amplitude of the echo is a nonlinear function of the amplitudes of the exciting pulses. There is no signal when any of the three pulses is absent.

It is because of the latter circumstance that we can refer to this echo signal as "anomalous." It has been reported[9] previously that polarization echo signals are excited in ferroelectrics near a phase transition, at the sum and difference frequencies of the exciting pulses ($\omega_1 \pm \omega_2 = \omega_e$). Each of the polarization echo signals in Ref. 2 was the result of excitation by two pulses, one of which could be one of the polarization echo signals. The echo observed in the present study, in contrast, is a result of the joint effects of all three rf pulses.

The following model is used in calculating the formation time of the anomalous echo.

(1) The first pulse may generate sound waves with frequencies $\omega/2$, ω, and 2ω simultaneously.
(2) During the second and third pulses, there may be a conversion of waves and a phase conjugation with generation of acoustic modes at all possible sum and difference frequencies, which can be denoted conveniently by $m\omega/2$, where $m=1,2,3,\ldots$.
(3) The conversion and phase conjugation[10] of the acoustic waves preserve the phase of each component in the spectrum of mode at the time of the conversion (or conjugation).

On the basis of this model, we can write the condition—the standard condition in echo theories—for phase matching of the spectral components as follows:

$$m_1\tau_1' \pm m_2\tau_2' = 4\tau_e'. \qquad (1)$$

Here τ_1' is the time scale of the loss of phase coherence of the first and second pulses, τ_2' is the time scale of the loss of phase coherence (or phasing in) of the second and third pulses; the numbers m_1 and m_2 determine the frequencies of the modes involved in shaping the echo; and the sign on m_2 specifies whether the mode transformed by the second pulse continues the phase coherence loss (+) or whether there is a phase conjugation (−) and, correspondingly, a phasing in. The procedure of determining the times τ_i' and τ_e' itself requires further justification. In the existing theoretical descriptions of the polarization echo in single crystals, it is customary to use the approximation that the exciting pulses are relatively short, and the loss of phase coherence which occurs during the pulses is ignored in calculations of the time required for the formation of the echo signals. In the experiments described here, the pulse lengths are comparable to the time intervals between pulses. It is therefore necessary to look at the experimental data on the echo formation time in order to draw conclusions about not only the nature of the frequency conversions and conjugations of the sound waves but also the nature of the loss of phase coherence of the field during the pulses. In other words, we need to decide whether to take τ_1', τ_2', and τ_e' in (1) to be simply the time intervals between pulses or whether we need to include the pulse lengths Δt_i, and if so in what order.

It was found from the results of seven series of experiments with various values of Δt_i, τ, and τ_1 that the formation time specified above for the anomalous echo,

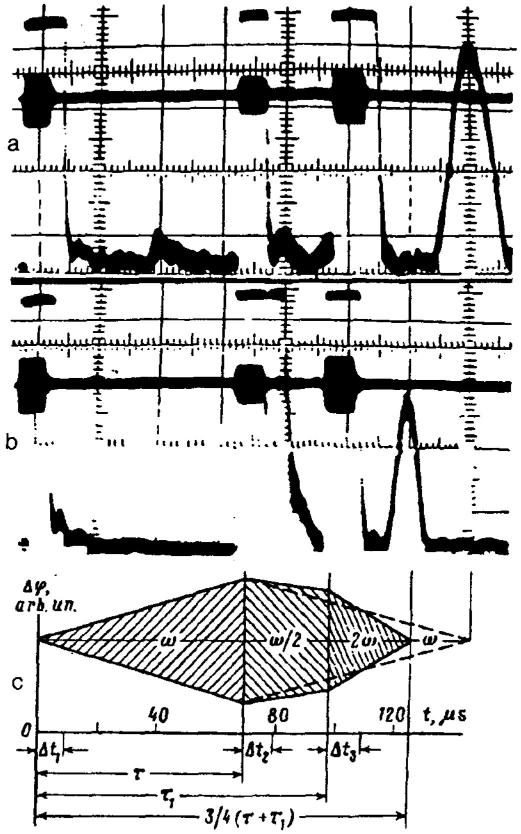

FIG. 2. Oscilloscope traces of the time sequences of rf pulses (ω, 2ω, ω) and of the induction and echo signals; diagram illustrating the formation of the anomalous echo. a—The receiver is tuned to the frequency ω; b—the receiver is tuned to the frequency 2ω (KDP single crystal, sweep time of 20 μs/cm, $E_{1,3}=1.3$, $E_2=1.1$, and $E_0=3.0$ kV/cm, $T=153.3$°C); c—diagram of the conversion of the acoustic modes during the formation of the anomalous echo.

$\tau_e=(3/4)(\tau+\tau_1)$, corresponds to experimental data within $\pm 2{,}3$ μs if we set $m_1=2$ and $m=-1$ in (1), and if we include the lengths of the rf pulses in the dephasing (or phasing) times τ_i'.

To get a clear picture of the processes by which the sound waves are transformed and the phases conjugated in the echo-formation process, it is convenient to use a diagram like that proposed previously by Bashkov.[11] Figure 2c shows a diagram of this sort for the formation of the anomalous echo of interest in the present letter. Plotted along the ordinate here is the deviation ($\Delta\varphi$) of the phase of the spectral component of the acoustic mode of interest from the mean value of the phase of the mode, as a function of the time. Two diverging (converging) rays represent the loss of phase coherence (phasing in) of two spectral components with a symmetric deviation of the frequencies ($\pm\Delta\omega$) from the mean value. The process depicted here consists of the following: 1) generation by the first rf pulse of a sound wave at the excitation frequency ω ($m_1=2$); 2) loss of phase coherence of this wave in the interval from 0 to τ; 3) conversion by the second rf pulse of this wave into the conjugate wave at the frequency $\omega/2$ ($m_2=-1$); 4) phasing of the conjugate wave in the interval from τ to τ_1 at a rate half the rate of the dephasing in the interval from 0 to τ, because of the halving of the frequency; 5) conversion of the wave by the third rf pulse into a wave with the frequency 2ω, without phase conjugation; 6) phasing of this wave in the interval from τ_1 to $(3/4)(\tau+\tau_1)$, at a rate twice the rate of the phase coherence loss in the interval from 0 to τ [the 4 on the right side of expression (1)].

This result demonstrates that nonlinearities of orders higher than those usually considered in the ferroelectric phase become important in the generation and conversion of acoustic modes near a ferroelectric phase transition.

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