# Study of the elastic nonlinearity of ferroelectrics with the help of hypersonic polarization echo signals in an ultrasonic field

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An experimental study has been made of the formation of a two-pulse hypersonic polarization echo in the field of an ultrasonic standing wave, using a single-domain $LiNbO_3$ sample. The plot of the intensity of the polarization echo as a function of the time interval between the exciting microwave pulses is found to be amplitude-modulated. The frequency of this modulation is determined by the ratio of the propagation velocities of the ultrasonic and hypersonic waves. A new model developed here can explain all aspects of the observed effect. The depth of the echo-signal modulation is shown to be associated with the nonlinear properties of the sample. Expressions are derived for the nonlinear elastic constants in terms of the modulation depth and the strain amplitude of the deformation of the crystal by the ultrasonic field. Measurements are used to evaluate the nonlinear elastic constant $C^{(3)}_{333313}$ for the $LiNbO_3$ sample.

## 1. INTRODUCTION

The polarization echo[1,2] is widely used to study the acoustic properties of ferroelectric samples, and is also used in experiments on acoustic paramagnetic resonance.[3] Since the intensity of the polarization echo depends on the nonlinear characteristics of the sample, it is interesting to examine the possibility of utilizing this phenomenon to determine the constants of the nonlinear piezoelectric effect and of the elastic nonlinearity of piezoelectric and ferroelectric materials. We have previously[4] studied the nonlinear piezoelectric effect. We studied how pulses of a static electric field affect the formation of the echo signals. In this paper we report an experimental and theoretical study of the elastic nonlinearity of ferroelectrics on the basis of the effect of the ultrasonic field of a standing wave on the intensity of the polarization echo signals.

## 2. EXPERIMENTAL PROCEDURE

The hypersonic polarization echo was excited at $T=4.2$ K by repeating pairs of microwave pulses at a carrier frequency of 9.6 GHz and duration $\sim 2\cdot 10^{-8}$ s. As the test sample we used a cubical single-domain $LiNbO_3$ crystal with sides 5 mm long. The faces of this cube were oriented perpendicular to the *x*, *y*, and *z* axes and were polished. The electric component of the pulsed microwave field from a coaxial resonator was applied to a face in the *xy* plane. Longitudinal hypersonic waves with a frequency of 9.6 GHz were excited in the sample as a result. After a time $2\tau$, where $\tau$ is the time interval between the first and second microwave pulses, a polarization echo signal arose. To study the effect of the ultrasonic field on the echo signals, we placed the sample in an effective capacitor, whose plates were oriented perpendicular to the crystallographic *y* axis (or *z* axis). In the former case, the application of the voltage from a cw rf oscillator to the pair of plates resulted in the excitation of transverse ultrasonic waves in the sample. In the latter case, the rf voltage excited a longitudinal ultrasonic wave. The pulsed microwave field exciting the echo signal reached the face of the crystal through a hole in the capacitor plate on the side of the microwave resonator. The frequency of the rf oscillator was chosen to be either 2.5 or 5 MHz. A minor adjustment of the frequency satisfied the conditions for exciting an ultrasonic standing wave in the sample. We then measured the intensity of the polarization echo as a function of the time interval between the microwave exciting pulses. In the presence of the ultrasonic field of the standing wave, the decrease in the echo signal $I(t)$ was intensity-modulated with a modulation period that depended on the ratio of the velocities of the ultrasonic and hypersonic waves.

## 3. THEORY

We first note that the polarization echo is the result of a phase conjugation of the first hypersonic pulse, which occurs in nonlinear piezoelectric materials because of a parametric interaction (in the case at hand, a three-wave interaction) of two counterpropagating hypersonic modes and the external microwave field (the second pulse) when certain phase relationships among the interacting modes are satisfied.[5] When a crystal with an elastic nonlinearity is deformed, the phase velocity of sound (of the hypersonic pulse in the case at hand) changes (Ref. 6, for example). If an ultrasonic standing wave is excited in a crystal, the conditions for phase conjugation of the first hypersonic pulse vary with the time interval ($\tau$) between the beginning of the first hypersonic pulse and the microwave electromagnetic pulse causing the conjugation. In other words, the conjugation conditions depend on the establishment of

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a standing ultrasonic strain wave in the part of the crystal in which the phase conjugation of the first hypersonic pulse occurs. The change in the phase velocity of the hypersonic pulse at the time of the phase conjugation disrupts the phase relations between the interacting modes of the second microwave pulse and the first hypersonic pulse.

To describe the effects of the modulation of the polarization-echo signal by the ultrasonic field, we expand the free energy of the nonlinear piezoelectric material in components of the strain tensor $U \equiv U_{ik} = 0.5(\partial_i U_k + \partial_k U_i)$ and the electric field $\mathbf{E}$. We consider the propagation of a hypersonic wave of frequency $\omega$ through the crystal. This wave is described by the displacement vector $U_i'$ under the condition that an ultrasonic field of frequency $\Omega$ $(\Omega \ll \omega)$, which is described by the displacement vector $\tilde{U}_i$, is excited in the crystal. We thus have $U_i = U_i' + \tilde{U}_i$. We also note that there are electric fields $E_i^\omega$ of the microwave pulse at the frequency $\omega$ in the crystal; i.e., we have $E_i = E_i^\omega(t)$. Using the approximation of a given electric-field pump wave $E_i^\omega$ and a given ultrasonic field $\tilde{U}_i$, we find

$$\partial_{tt} U_i' - s^2 \partial_{xx} U_i'$$
$$= \rho^{-1} [C^{(3)}_{ijklmn} \tilde{U}_{mn} + f_{mnijkl} E_m^\omega E_n^\omega] \partial_{jl} U_k'. \tag{1}$$

Here $\rho$ is the density of the crystal, $s$ is the velocity of the hypersonic wave, and $C^{(3)}$ and $f$ are the nonlinear elastic tensor and the electrostriction tensor, respectively (we omit tensor indices). In deriving (1), we included on the right-hand side only those terms that made contributions $\propto \exp(i\omega t)$. Here we assume that $\tilde{U}_{mn}$ is a slowly varying quantity, since we have $\Omega \ll \omega$.

We analyzed an equation like (1) in Ref. 4. The difference between Eq. (1) of the present paper and the corresponding equation of Ref. 4 [Eq. (3) of that paper] is that a term $\propto C^{(3)} \tilde{U}$, which describes a slowly varying elastic field $\tilde{U}$, appears in brackets on the right side of Eq. (3) of Ref. 4, instead of the slowly varying first term $\propto \eta E$. Taking $U_i'$ to be of the form determined by the same relations between the direct and conjugate hypersonic waves as in Eq. (4) of Ref. 4, we find an equation for the slowly varying amplitudes, in which we must take $\Delta F_{1(2)} = F_{1(2)}(z,t) - F_1(0,0)$ to be

$$F_1(z,t) = \frac{C^{(3)}_{ijklmn} \tilde{U}_{mn}}{2\rho s^2} k_j^0 k_l^0 q_i^{(1)} q_k^{(1)} \omega, \tag{2}$$
$$|\mathbf{k}^0| = 1, \quad (\mathbf{k}^0 k) = \mathbf{k}, \quad \omega = ks.$$

The quantity $\mathbf{k}$ in (2) is the wave vector of the first hypersonic pulse, and $\mathbf{q}^{(1)}$ and $\mathbf{q}^{(2)}$ are the polarization vectors of the first and conjugate hypersonic waves. Using a change of variables like that in (8), (9) in Ref. 4, we find equations for the reduced amplitudes $\bar{U}_1$ and $\bar{U}_2$ of the direct and conjugate hypersonic pulses:

$$\partial_z \bar{U}_1 + s^{-1} \partial_t \bar{U}_1 = a \exp\left[ -is \int_{t_0}^{t} \Delta F(z,t;t')\, dt' \right] \bar{U}_2^*, \tag{3}$$

$$\partial_z \bar{U}_2 - s^{-1} \partial_t \bar{U}_2 = -a \exp\left[ -is \int_{t_0}^{t} \Delta F(z,t;t')\, dt' \right] \bar{U}_1^*,$$
$$\Delta F(z,t;t') = \Delta F_1(z - st + st', t') + \Delta F_2(z + st - st', t'). \tag{4}$$

The coefficient $a$ describes the parametric interaction of the direct and conjugate microwave modes at the time at which the second microwave pulse is applied if external agents are ignored (i.e., in the case $\Delta F = 0$). If there is an ultrasonic field $\tilde{U}$ in the crystal at the time at which the second microwave pulse is applied $(\Delta F \neq 0)$, a phase modulation of the hypersonic wave will be phase-modulated, and the efficiency of the parametric phase conjugation will decrease because of a disruption of phase matching.[7]

We make use of the circumstance that in polarization-echo experiments the conjugate electromagnetic-field pulse is short, and $|\bar{U}_2| \ll |\bar{U}_1|$ ($\bar{U}_2$ is several orders of magnitude smaller than $\bar{U}_1$). Under these conditions we can set the right side of Eq. (3) equal to zero, and $\bar{U}_2$ will be determined by Eq. (4). Here we will have $\bar{U}_1 = \bar{U}_2(z - st)$. We make the change of variables $z = \nu - s\theta$, $t = \theta$, in (4). For $\bar{U}_2$ we then find

$$\bar{U}_2 = -as \int_{t/2}^{t/2+\Delta t} \bar{U}_1^*(\nu - 2s\theta)$$
$$\times \exp\left[ -is \int_{t/2}^{\theta} \Delta F(\nu - s\theta, \theta; t')\, dt' \right] d\theta. \tag{5}$$

The integration limits in (5) are $t/2$ and $t/2 + \Delta t$, where $\Delta t$ is the length of the conjugating microwave pulse. We put the beginning of the conjugating pulse at the time $t/2$ for convenience and in order to transform the time at which the echo signal appears to the time $t$. Setting $\bar{U}_1(\nu - 2s\theta) = \bar{U}_1(0) = \text{const}$ during the conjugating microwave pulse, we find an expression for the intensity of the polarization echo, $I(t,\alpha)$:

$$I(t,\alpha) = I_0 e^{-2\Gamma t} \varphi(t,\alpha), \tag{6}$$

$$\varphi(t,\alpha) = \left| \int_{t/2}^{t/2+\Delta t} \exp\left[ -is \int_{t/2}^{\theta} \Delta F(\nu - s\theta, \theta; t')\, dt' \right] \right.$$
$$\left. \times \frac{d\theta}{\Delta t} \right|^2. \tag{7}$$

Here $I_0 e^{-2\Gamma t}$ is the intensity of the polarization-echo signal in the absence of the elastic field of the ultrasonic wave,

$$I_0 = |a U_1(0,0) \Delta t|^2.$$

In (7) we must set $\nu = z + st/2 = st/2 + st/2 = st$. In (6) and (7) we have introduced the parameter $\alpha$, which is the initial phase of the ultrasonic elastic wave, on which $\tilde{U}_i$ depends.

The ultrasonic elastic wave has its greatest effect on the shaping of the polarization-echo signal when an ultrasonic standing wave forms in the crystal, i.e., in the case of an acoustic resonance for the given crystalline sample. If the standing wave is excited in a crystal with free ends, the displacement field $\tilde{U}_i$ of this wave is

$$\tilde{U}_i \cong A e_i \cos(k^\Omega z) \cos(\Omega t + \alpha), \quad k^\Omega = \Omega / s_\Omega, \tag{8}$$

where $A$, $\mathbf{e}$, and $s_\Omega$ are the amplitude, polarization vector, and propagation velocity of the ultrasonic elastic wave. Substituting (8) into (2), we find $\Delta F(\nu - s\theta, \theta; t')$ with $\nu = st$:

$$\Delta F(\nu - s\theta,\theta;t')\,|_{\nu=st} = 2s^{-1}\Omega\Delta t F_0 \chi(t,\theta,t',\alpha), \qquad (9)$$

$$\chi(t,\theta,t',\alpha) = \sin\left[\Omega \frac{s}{s_\Omega}(t-\theta)\right] \times \cos\left[\Omega \frac{s}{s_\Omega}(t'-\theta)\right]\cos(\Omega t' + \alpha), \qquad (10)$$

$$F_0 = -\frac{C^{(3)}_{ijklmn}\omega A}{\rho s^2 s_\Omega} k^0_j k^0_l q^{(1)}_i q^{(1)}_k e_m k^0_n. \qquad (11)$$

It can be seen from (9) and (10) that the intensity of the ultrasound-modulated polarization-echo signal depends on $\alpha$. Experimentally, one usually observes an echo signal resulting from a superposition of a series of triggering and conjugating microwave pulses, distributed in pairs at time intervals of $\tau = t/2$, so that for each pair of such pulses the initial phase $\alpha$ of the elastic wave will be different. In other words, one observes an echo signal averaged over $\alpha$. Substituting (10) into (7), and averaging $\varphi(t,\alpha)$ over $\alpha$, we finally find the following expression for the polarization-echo signal modulated by the ultrasonic standing wave:

$$I(t) = I_0 e^{-2\Gamma t}\varphi(t), \quad \varphi(t) = \overline{\varphi(t,\alpha)},$$

$$\varphi(t,\alpha) = \left| \int_{t/2}^{t/2+\Delta t} \frac{d\theta}{\Delta t} \exp[i2\Omega\Delta t F_0 \times \int_{t/2}^{\theta} \chi(t,\theta,t',\alpha)\frac{dt'}{\Delta t}]\right|^2. \qquad (12)$$

The overbar in (12) denotes an average over $\alpha$. The average is taken after $\varphi(t,\alpha)$ is determined. After an elementary integration over $dt'$, the integration over $d\theta$ and the subsequent averaging over $\alpha$ are carried out numerically. However, we can immediately specify the periodicity of the modulating factor $\varphi(t)$: the maximum modulation depth should be observed at those instants at which the conjugate pulse arrives from regions of the crystal corresponding to antinodes of the standing wave. Since the antinodes repeat at half the wavelength of the ultrasonic elastic wave, $\lambda_\Omega$, the temporal period of $\varphi(t)$ is

$$T_M = 2\frac{\lambda_\Omega}{2}\frac{1}{s} = \frac{s_\Omega}{s}\frac{2\pi}{\Omega}. \qquad (13)$$

Observation of the period $T_M$ provides an additional opportunity to monitor the type of excited mode of the ultrasonic elastic wave, since the velocity $s$ can be found directly from the microwave measurements.

## 4. DISCUSSION

To determine the depth and nature of the modulation of the polarization-echo signal by the ultrasonic elastic field, we need to know the amplitude of the ultrasonic standing wave, $A$. The calculation of $A$ depends on the electrical and mechanical boundary conditions for the excitation of a certain type of wave in a specific sample.[5]

For a transverse ultrasonic standing elastic wave along the $Oz$ direction we have[8]

$$A_S = \frac{2d_{15}V_0 s_\Omega}{\gamma\Omega l^2}, \qquad (14)$$

while for a longitudinal standing wave in the $Oz$ direction we have[8]

$$A_L = \frac{s^D_{33}V_0}{\gamma l g^D_{33}}. \qquad (15)$$

In (14) and (15) we use the following notation: $d_{15}$ and $g^D_{33}$ are piezoelectric coefficients for a certain $E$ and a certain $D$ ($D$ is the electric displacement), $s^D_{33}$ is a component of the elastic compliance tensor for a certain $D$, $l$ is the length of the sample, $V_0$ is the amplitude of the potential difference across the capacitor plates $[V = V_0\exp(i\Omega t)]$, and $\gamma$ is the imaginary part of the wave vector $\mathbf{k}_\Omega$, which reflects the attenuation of the ultrasound (either transverse or longitudinal). Tuning to resonance is carried out by varying the frequency of the external electric field. The relative change in frequency is $\Delta\Omega/\Omega = \lambda_\Omega/2l = \pi s_\Omega/l\Omega$.

Setting $s_\Omega = 3.5 \cdot 10^5$ cm/s in (14) and (15) for the transverse ultrasonic wave, $s_\Omega = s = 7.3 \cdot 10^5$ cm/s for the longitudinal ultrasonic wave, $d_{15} = 2 \cdot 10^{-6}$ esu, $g^\partial_{33} = 8 \cdot 10^{-8}$ esu (Ref. 9), $s^D_{33} = 0.87 \cdot 10^{-12}$ cm$^2$/dyn, $l = 0.5$ cm, $V_0 = 10$ V/cm, $\Omega = 2\pi \cdot 5 \cdot 10^6$ s$^{-1}$, and $\gamma = 2 \cdot 10^{-5}$ cm$^{-1}$, we find $A_S = 8 \cdot 10^{-4}$ cm and $A_L = 3 \cdot 10^{-2}$ cm for the transverse and longitudinal waves, respectively.

We ignored edge effects in deriving Eqs. (14) and (15). These equations are valid only for an approximate estimate of the amplitude $A$.

It can be seen from (11) that by using various types of hypersonic and ultrasonic modes, and by studying the nature and depth of the modulation of the polarization-echo signal by the ultrasonic elastic wave, we can evaluate the nonlinear elastic constants $C^{(3)}_{ijklmn}$. In the present experiment, for example, we can evaluate the constants $C^{(3)}_{333333}$ and $C^{(3)}_{333313}$. Figures 1 and 2 show the results of numerical calculations of the amplitudes of the polarization-echo signals modulated by a transverse wave (Fig. 1) and by a longitudinal one (Fig. 2) for various values of $F_0$ ($F_0 = 5$ corresponds to $A = 2 \cdot 10^{-4}$ cm, $\Omega = 2\pi \cdot 5 \cdot 10^6$ s$^{-1}$, $\Delta t = 2 \cdot 10^{-8}$ s, and $C^{(3)}_{333333} \approx C^{(3)}_{333313} \cong 10^{12}$ esu; Ref. 10). With increasing $F_0$, the modulation depth increases. The polarization-echo signal is not restored even at times corresponding to phase conjugation from those regions of the crystal in which the amplitude of the ultrasonic standing wave is zero (from the nodes of the standing wave). The reason is that in time $\Delta t$, the hypersonic pulse covers a region of width $s_\Omega \Delta t$ in the crystal. If $\Delta t$ is comparable to one half-period of the ultrasonic wave, the modulation is smoothed over.

Figure 3 compares experimental values of the modulation of the polarization-echo signal by a transverse ultrasonic standing wave with results calculated from Eq. (12).

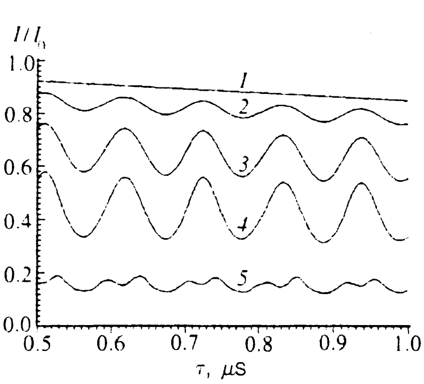


FIG. 1. Modulation of the amplitude of the polarization echo by a transverse ultrasonic wave as calculated from Eq. (12) with $\Omega=2\pi\cdot5\cdot10^6\ s^{-1}$ and $\Delta t=2\cdot10^{-8}$ s. *1)* $F_0=0$; *2)* 1; *3)* 2; *4)* $\pi$; *5)* $2.5\pi$.

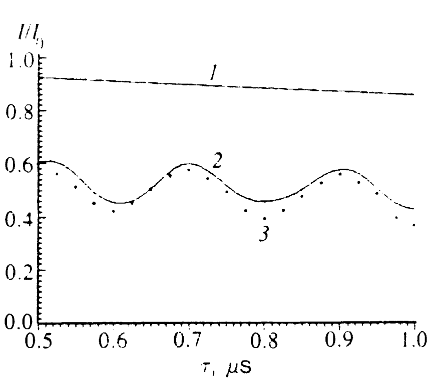


FIG. 3. Amplitude modulation of the polarization echo by a transverse ultrasonic wave as calculated from Eq. (12) with $F_0=0$ (*1*) and 5.4 (*2*). $\Omega=2\pi\cdot2.5\cdot10^6\ s^{-1}$. Curve *3*: Experimental values of the modulation of the polarization-echo signal by a transverse ultrasonic wave. With $\Omega/2\pi=2464$ kHz, $V_0=10$ V/cm, and $\Delta t=2\cdot10^{-8}$ s, the modulation frequency is $1/T_M=5012$ kHz.

The experimental data on the modulation of the polarization-echo signal by an ultrasonic field were obtained for $\Omega=2\pi\cdot2.5\cdot10^6\ s^{-1}$, $\Delta t=2\cdot10^{-8}$ s, and $F_0=5.4$ (this situation corresponds to $C^{(3)}_{333313}\approx10^{12}$ esu at $V_0=10$ V/cm).

Since the ratio of the velocities of a longitudinal hypersonic wave and a transverse ultrasonic wave in $LiNbO_3$ is $s/s_\Omega\approx2$, the modulation frequency should be close to twice the ultrasound frequency according to Eq. (13). We also know that when ultrasound at frequency $\Omega$ is excited in a sample, the second harmonic $2\Omega$ is generated. It was thus necessary to verify that the modulation of the polarization echo was not caused by the frequency $2\Omega$. Evidence that it was not comes from the fact that the experiments show no modulation at the fundamental frequency $\Omega$, at which the strain amplitude is much higher than at twice this frequency. The modulation frequency was determined with the help of an I2-26 time-interval meter. An ultrasonic standing wave was established in the sample beforehand by varying the frequency of the rf oscillator over a narrow interval. The frequency, measured by a ChZ-64 frequency counter, was 2464 kHz. The measured modulation frequency was 5012 kHz, which agrees with Eq. (13) and which differs by 84 kHz from twice the frequency of the ultrasound.

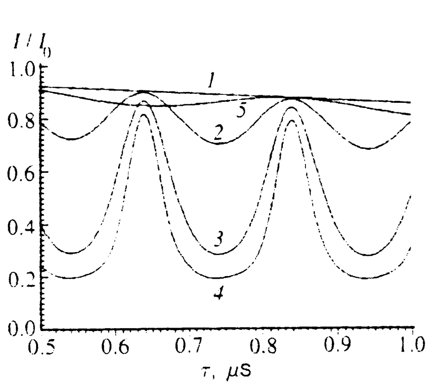


FIG. 2. Amplitude modulation of the polarization echo by a longitudinal ultrasonic wave as calculated from Eq. (12) with $\Delta t=2\cdot10^{-8}$ s. *1)* $F_0=0$; *2)* 2; *3)* 5; *4)* $2.5\pi$ ($\Omega=2\pi\cdot5\cdot10^6\ s^{-1}$); *5)* 2 ($\Omega=2\pi\cdot2.5\cdot10^6\ s^{-1}$).

It can be seen from these results that the polarization-echo method can be used to determine the nonlinear elastic constants of piezoelectric and ferroelectric materials. The accuracy of the method can be improved through independent measurements of the amplitude of the ultrasonic standing wave. We also note that conjugation of the hypersonic pulse in the presence of an ultrasonic standing wave can be arranged to occur in any part of the crystal by choosing the appropriate time to apply the second microwave pulse. This method can thus be used to determine the nonlinear elastic constants in various parts of a crystal. The resolution in terms of the spatial position of the region under study will improve as the microwave pulses are narrowed.


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